



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|--|-----------|--|
| (51) International Patent Classification ⁶ : C11D | A2 | (11) International Publication Number: WO 00/02981 (43) International Publication Date: 20 January 2000 (20.01.00) |
| (21) International Application Number: PCT/US99/15666 (22) International Filing Date: 12 July 1999 (12.07.99) (30) Priority Data: 98870226.2 10 July 1998 (10.07.98) EP 98870155.3 28 October 1998 (28.10.98) EP (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BETTIOL, Jean-Luc, Philippe [FR/BE]; 93, avenue Slegers, B-1200 Brussels (BE). BUSCH, Alfred [DE/BE]; Handelsstraat 210, B-1840 Londerzeel (BE). DENUTTE, Hugo [BE/BE]; Molenstraat 12, B-9308 Hofstade (BE). LAUDAMIEL, Christophe [FR/BE]; 20A, rue de la Violette, B-1000 Brussels (BE). SMETS, Johan [BE/BE]; Bollenberg 79, B-3210 Lubbeek (BE). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US). | | (81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i> |
| (54) Title: LAUNDRY AND CLEANING COMPOSITIONS | | |
| (57) Abstract | | |
| <p>The present invention relates to a laundry and cleaning composition comprising a detergent ingredient and a product of reaction between a primary and/or secondary amine and a perfume component. By the present invention, there is obtained a release of the active component over a longer period of time than by the use of the active itself.</p> | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|----|--------------------------|----|--|----|--|----|--------------------------|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | ML | Mali | TR | Turkey |
| BG | Bulgaria | HU | Hungary | MN | Mongolia | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MR | Mauritania | UA | Ukraine |
| BR | Brazil | IL | Israel | MW | Malawi | UG | Uganda |
| BY | Belarus | IS | Iceland | MX | Mexico | US | United States of America |
| CA | Canada | IT | Italy | NE | Niger | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NL | Netherlands | VN | Viet Nam |
| CG | Congo | KE | Kenya | NO | Norway | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NZ | New Zealand | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | PL | Poland | | |
| CM | Cameroon | KR | Republic of Korea | PT | Portugal | | |
| CN | China | KZ | Kazakhstan | RO | Romania | | |
| CU | Cuba | LC | Saint Lucia | RU | Russian Federation | | |
| CZ | Czech Republic | LI | Liechtenstein | SD | Sudan | | |
| DE | Germany | LK | Sri Lanka | SE | Sweden | | |
| DK | Denmark | LR | Liberia | SG | Singapore | | |
| EE | Estonia | | | | | | |

LAUNDRY AND CLEANING COMPOSITIONS

Field of the invention

The present invention relates to laundry and cleaning compositions comprising a product of reaction between an amine and a perfume component, in particular aldehyde or ketone perfumes.

Background of the invention

Laundry and cleaning products are well-known in the art. However, consumer acceptance of laundry and cleaning products is determined not only by the performance achieved with these products but also by the aesthetics associated therewith. The perfume components are therefore an important aspect of the successful formulation of such commercial products.

It is also desired by consumers for laundered fabrics to maintain the pleasing fragrance over time. Indeed, perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume carried-over from an aqueous laundry bath onto fabrics is often marginal and does not last long on the fabric. Furthermore, fragrance materials are often very costly and their inefficient use in laundry and cleaning compositions and ineffective delivery to fabrics results in a very high cost to both consumers and laundry and cleaning manufacturers. Industry, therefore, continues to seek with urgency for more efficient and effective fragrance delivery in laundry and cleaning products, especially for improvement in the provision of long-lasting fragrance to the fabrics.

One solution is to use carrier mechanisms for perfume delivery, such as by encapsulation. This is taught in the prior art and described in U.S. 5,188,753.

Still another solution is to formulate compounds which provide a delayed release of the perfume over a longer period of time than by the use of the perfume itself. Disclosure of such compounds may be found in WO 95/04809, WO 95/08976 and co-pending application EP 95303762.9.

However, notwithstanding the advances in the art, there is still a need for a compound which provides a delayed release of the perfume component.

That need is even more acute for perfume ingredients which are characteristic of the fresh notes, namely the aldehydes and ketones perfume ingredients. Indeed, whilst these provide a fresh fragrance, these perfumes are also very volatile and have a low substantivity on the surface to be treated like fabrics.

Accordingly, it is a further object of the invention to provide a laundry and cleaning composition comprising a perfume component which provides a fresh fragrance and is substantive to the treated surface.

The Applicant has now found that specific reaction products of amine compounds with an active aldehyde or ketone, such as imines compounds, also provide a delayed release of the active such as a perfume.

Imine compounds are known in the art under the name of Schiff bases which is the condensation of an aldehyde perfume ingredient with an anthranilate. A typical description can be found in US 4853369. By means of this compound, the aldehyde perfume is made substantive to the fabrics. However, a problem encountered with these schiff bases is that the methylantranilate compound also exhibits a strong scent, which as a result produces a mixture of fragrances, thereby reducing or even inhibiting the aldehyde fragrance perception.

To achieve such perfume composition with comparable aldehyde or ketones fresh notes whilst still having satisfactory fabric substantivity, perfumers have formulated around the composition. For example, by having a carrier or

encapsulating material for such notes such as with cyclodextrin, zeolites or starch.

Still another solution is the use of a glucosamine as described in JP 09040687. However, this compound has been found to give a very low stability in the wash/cleaning process. As a result, insufficient perfume residuality on the treated fabric and/or hard surface has been found with these glucosamine compounds.

A further solution is described in Chemical release control, Kamogawa et Al., J. Poly. Sci. . Polym. Chem. Ed. Vol 20, 3121 (1982) which describe the use of amino styrene compounds condensed with aldehydes perfumes, whereby the release of the perfume is triggered by means of copolymerisation or acidification of the compound. Its use in laundry and cleaning product is however not mentioned.

The Applicant has now found that a reaction product between a specific primary and/or secondary amine -containing compound and a perfume component also fulfill such a need.

Another advantage of the compounds of the invention is their ease of manufacture rendering their use most desirable.

Summary of the invention

The present invention relates to a laundry and cleaning composition comprising a deterative ingredient and a product of reaction between a primary and/or secondary amine containing compound and a perfume component selected from ketone, aldehyde, and mixtures thereof, characterised in that said amine containing compound has an Odor Intensity Index of less than that of a 1% solution of methylanthranilate in dipropylene glycol, and the product of reaction a Dry Surface Odor Index of more than 5.

In a further aspect of the invention, there is provided a method of delivering residual fragrance to a surface by means of the compound or composition of the invention.

Detailed description of the invention

I-Product of reaction between a compound containing a primary and/or secondary amine functional group and a perfume component

An essential component of the invention is a product of reaction between a compound containing a primary and/or secondary amine functional group and a perfume component, so called hereinafter "amine reaction product".

A-Primary and/or secondary amine

By "primary and/or secondary amine", it is meant a component which carries at least one primary and/or secondary amine and/or amide function.

The primary and/or secondary amine compound is also characterized by an Odor Intensity Index of less than that of a 1% solution of methylantranilate in dipropylene glycol.

Odor Intensity Index method

By Odor Intensity Index, it meant that the pure chemicals were diluted at 1% in Dipropylene Glycol, odor-free solvent used in perfumery. This percentage is more representative of usage levels. Smelling strips, or so called "blotters", were dipped and presented to the expert panellist for evaluation. Expert panellists are assessors trained for at least six months in odor grading and whose gradings are checked for accuracy and reproducibility versus a reference on an on-going basis. For each amine compound, the panellist was presented two blotters: one reference (Me Anthranilate, unknown from the panellist) and the sample. The panellist was asked to rank both smelling strips on the 0-5 odor intensity scale, 0 being no odor detected, 5 being very strong odor present.

Results:

The following represents Odor Intensity Index of an amine compound suitable for use in the present invention and according to the above procedure. In each

case, numbers are arithmetic averages among 5 expert panellists and the results are statistically significantly different at 95% confidence level:

| | |
|----------------------------------|-----|
| Methylantranilate 1% (reference) | 3.4 |
| Ethyl-4-aminobenzoate (EAB) 1% | 0.9 |

A general structure for the primary amine compound of the invention is as follows:



wherein B is a carrier material, and n is an index of value of at least 1.

Compounds containing a secondary amine group have a structure similar to the above excepted that the compound comprises one or more -NH- groups instead of -NH₂. Further, the compound structure may also have one or more of both -NH₂ and -NH- groups.

Preferred B carriers are inorganic or organic carriers.

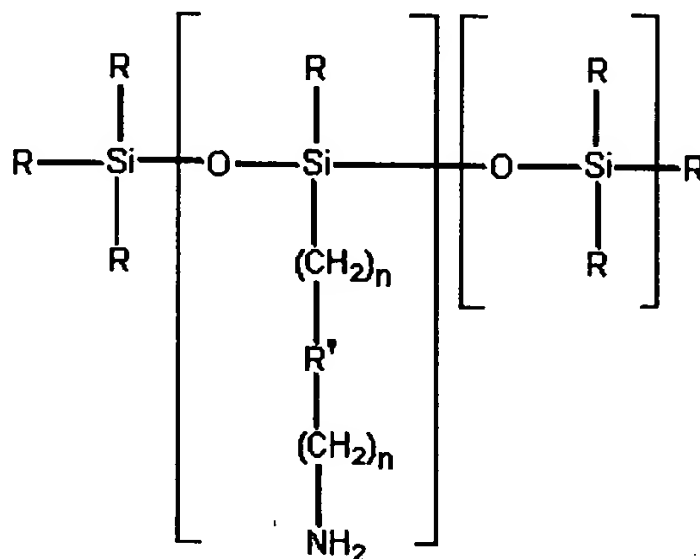
By "inorganic carrier", it is meant a carrier which is non-or substantially non carbon based backbones.

Among the inorganic carriers, preferred inorganic carriers are mono or polymers or organic-organosilicon copolymers of amino derivatised organo silane, siloxane, silazane, alumane, aluminum siloxane, or aluminum silicate compounds. Typical examples of such carriers are: organosiloxanes with at least one primary amine moiety like the diaminoalkylsiloxane [H₂NCH₂(CH₃)₂Si]O, or the organoaminosilane (C₆H₅)₃SiNH₂ described in: Chemistry and Technology of Silicone, W. Noll, Academic Press Inc. 1998, London, pp 209, 106).

Mono or polymer or organic-organosilicon copolymers containing one or more organosilylhydrazine moiety are also preferred. A typical example of such a class of carrier material is the N,N'-bis(trimethylsilyl)hydrazine (Me₃Si)₂NNH₂ described in: The OrganoSilicon Chemistry Second international Symposium, Pure and Applied Chemistry, Vol, 19 Nos 3-4, (1969).

The following are also preferred mono or poly silazanes and which are exemplified by the 1,1,1,3,3,3,-hexamethyl-2-phenyldiaminosilyldisilasane $[(CH_3)_3Si]_2NSi(C_6H_5)NH_2$ 2 described in: *OrganoSilicon Compounds*, 1965, V. Bazant and al. Academic Press). Still other preferred examples of polymer silicone derivatives are the cyclic 1,1,5,5,7,7,7,11,11-Octamethyl-3-9-bis-[2-(2-aminoethylamino)-ethyl]-1,5,7,11-tetrasiloxane-3,9-diaza-6,12-dioxacyclododecane and the Hexaethoxydiamino cyclotetrasiloxane $(C_6H_5)(NH_2)_2Si_4O_4$, id, Vol 2 part 2, p 474, p454).

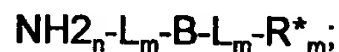
Preferred amino functionalized inorganic polymeric carriers for use herein are polyaminoalkyl polysiloxanes. Typical disclosure can be found in JP 79,131,096, and EP 058 493. Still other inorganic polymeric carriers suitable for use herein are the amino functionalized polydi-alkylsiloxanes, as described in EP 150 867 and having the general formula:



Wherein $R = C_{1-16}$ preferentially C_{1-4} alkyl; n is an integer from 0 to 16 preferentially from 1 to 6, $R' = \text{nil}, O, C=O, COO, NC=O, C=O-NR, NR, SO_m$, $m=2,3$.

By organic carriers, it is meant carriers having essentially carbon bond backbones. Typical amines having organic carrier include aminoaryl derivatives, polyamines, aminoacids and derivatives, substituted amines and amides, glucamines, dendrimers and amino-substituted mono-, di-, oligo-, poly-saccharides.

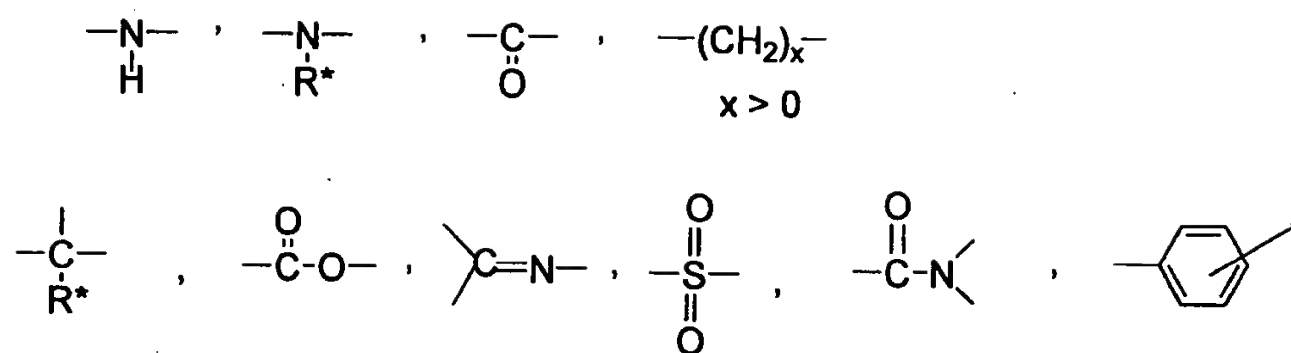
Of course, the amine compound can be interrupted or substituted by linkers or cellulose substantive group. A general formula for this amine compound may be represented as follows:



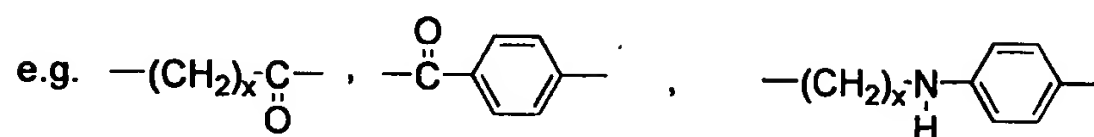
wherein each m is an index of value 0 or at least 1, and n is an index of value of at least 1 as defined herein before. As can be seen above, the amine group is linked to a carrier molecule as defined by classes hereinafter described. The primary and/or secondary amine group is either directly linked to the carrier group or via a linker group L. The carrier can also be substituted by a R* substituent, and R* can be linked to the carrier either directly or via a linker group L. Of course, R* can also contain branching groups like e.g. tertiary amine and amide groups.

It is important for the purpose of the invention that the amine compound comprises at least one primary and/or secondary amine group to react with the perfume aldehyde and/or ketone to form the reaction products. Of course, the amine compound is not limited to having only one amine function. Indeed, more preferably, the amine compound comprises more than one amine function, thereby enabling the amine compound to react with several aldehydes and /or ketones. Accordingly, reaction products carrying mixed aldehyde(s) and/or ketone(s) can be achieved, thereby resulting in a mixed release of such fragrances.

Typical linker group include:



L can also be a combination



L can also contain —O— if this group is not directly linked to N

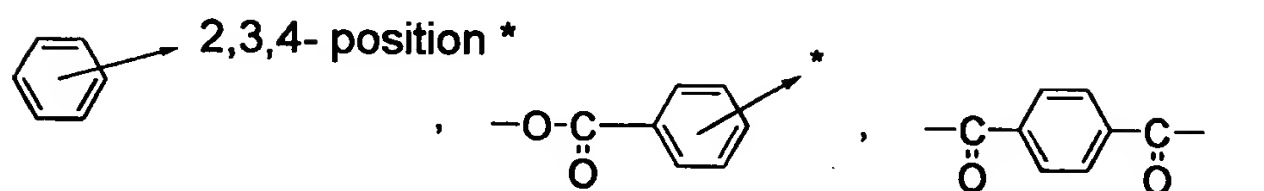
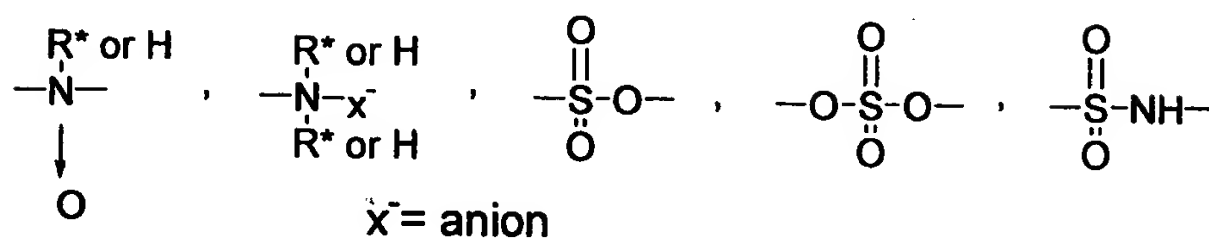
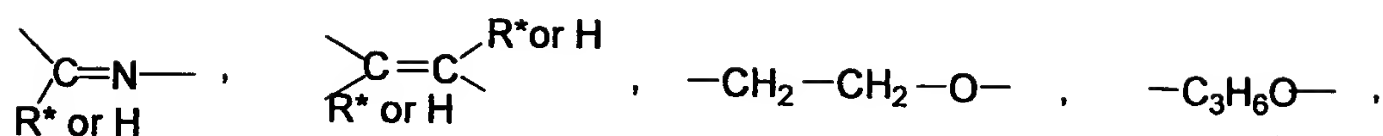
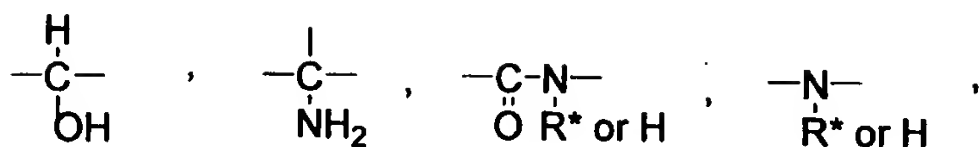
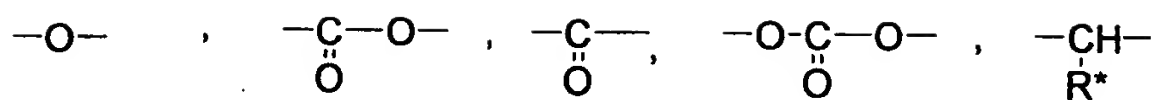


Most of the compounds described in the classes of amine compounds hereinafter will contain at least one substituent group classified as R*.

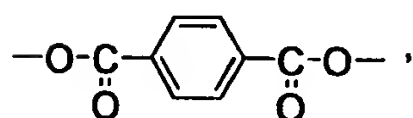
R* contains 1 to 22 carbon atoms in the main chain and optionally can be an alkyl, alkenyl, or alkylbenzene chain. It can also contain alicyclic, aromatic, heteroaromatic or heterocyclic systems, either inserted into the main chain or by substitution of an H atom of the main chain. Further, R* can either be linked to the carrier B material or via a linker L, as defined herein before. In this instance, L can also be —O— .

The main chain can contain from 1 to up to 15 R* groups.

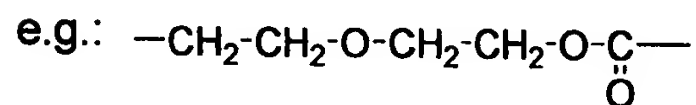
Typical R* insertion groups include:



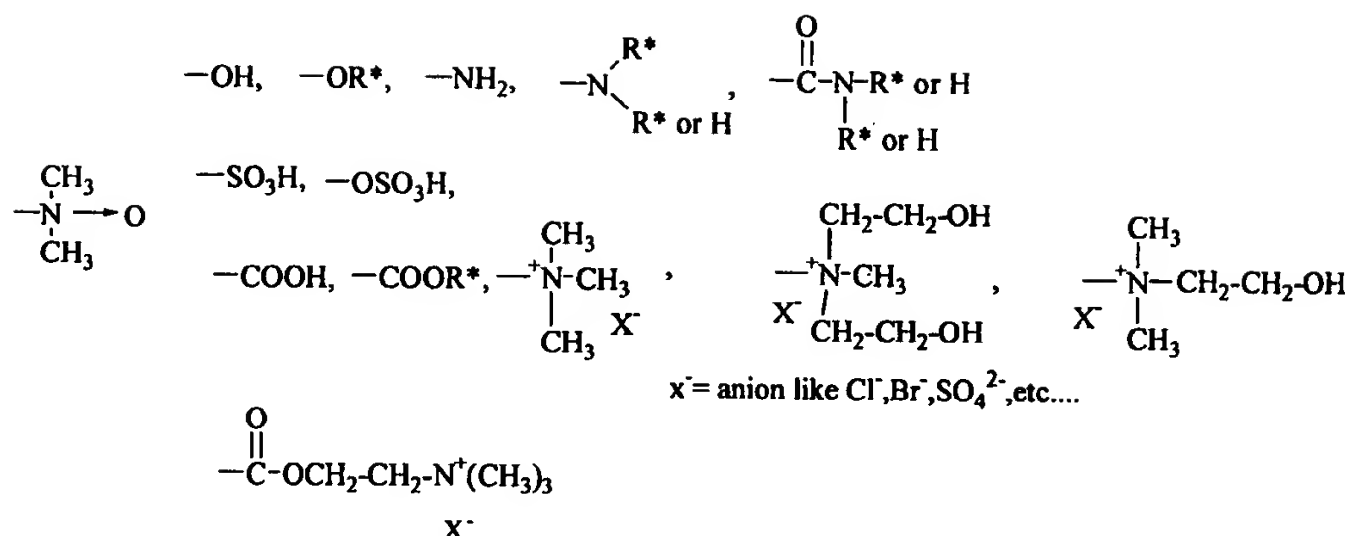
* the arrow indicates upto 3 substitutions in position 2,3,4



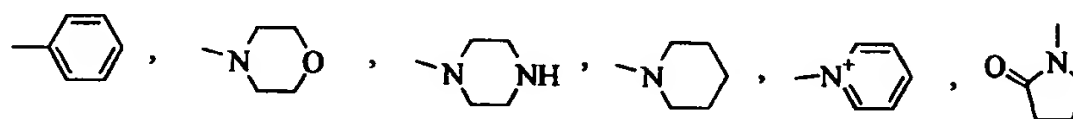
R^* can also contain several insertion groups linked together. e.g.



Furthermore, R^* can carry a functional end group E that provides additional surface substantivity. Typical organic groups of this end group include:

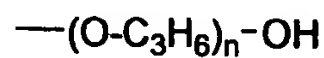
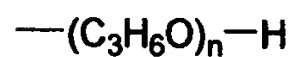
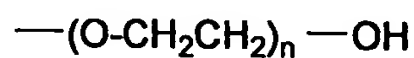


E can also be an aromatic, alicyclic, heteroaromatic, or heterocyclic group including mono-, di-, oligo-, polysaccharides



In addition, the R* group can also be modified via substitution of one or more H atoms in the main chain. The substitution group can either be E or the insertion groups as defined above where the insertion group is terminated by any of H, E, or R*.

R* can also be a group made of ethoxy or epoxy groups with n ranging from 1 to 15, including groups like:



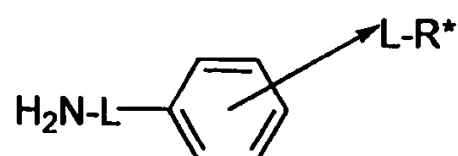
As defined herein before, preferred amine having organic carrier material B may be selected from aminoaryl derivatives, polyamines, aminoacids and derivatives, substituted amines and amides, glucamines, dendrimers, amino-substituted mono-, di-, oligo- polysaccharides and/or mixtures thereof.

1-Amino aryl derivatives

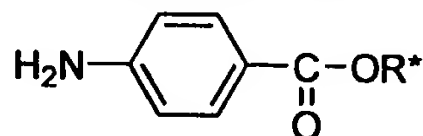
In this class of compounds, the amino group is preferably attached to a benzene ring. The benzene ring is further substituted in the para- and/or meta-position with R* as defined herein before. R* can be attached to the benzene ring via a linker L. The benzene ring can be substituted by other aromatic ring systems including naphthalene, indole, benzimidazole, pyrimidine, purine, and mixture thereof.

Preferably, the R* is attached to the benzene ring in its para position.

Typical amino-benzene derivatives have the following formula:



Preferred amino-benzene derivatives have the following formula:



Preferred amino-benzene derivatives are alkyl esters of 4-amino benzoate compounds, preferably selected from ethyl-4-amino benzoate, phenylethyl-4-aminobenzoate, phenyl-4-aminobenzoate, 4-amino-N'-(3-aminopropyl)-benzamide, and mixtures thereof.

2-Polyamines

The polyamines of the invention need to have at least one, preferably more than one free and unmodified primary and/or secondary amine group, to react with the perfume aldehyde or ketone. In the polyamines, H can be substituted by R*, optionally via a linker group L. Additionally, the primary and/or secondary amine group can be linked to the polymer end via a linker group L.

The polyamines compounds suitable for use in the present invention are water-soluble or dispersible, polyamines. Typically, the polyamines for use herein have a molecular weight between 150 and 2×10^6 , preferably between 400 and 10^6 , most preferably between 5000 and 10^6 . These polyamines comprise backbones

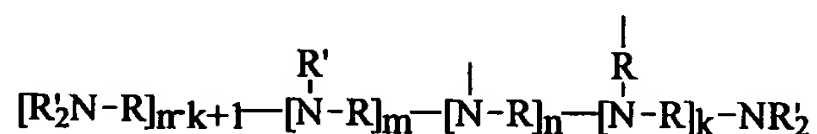
that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree. Preferably, the polyamine backbones described herein are modified in such a manner that at least one, preferably each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

For the purposes of the present invention the term "modification" as it relates to the chemical structure of the polyamines is defined as replacing a backbone -NH hydrogen atom by an R' unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an R' unit. Quaternization or oxidation may take place in some circumstances without substitution, but substitution is preferably accompanied by oxidation or quaternization of at least one backbone nitrogen.

The linear or non-cyclic polyamine backbones that comprise the polyamine have the general formula:



The cyclic polyamine backbones that comprise the polyamine have the general formula:



The above backbones prior to optional but preferred subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure

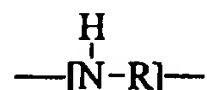


is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure



is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure



is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure



is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all of the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W

and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

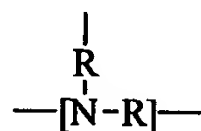
The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



for linear polyamine and by the general formula



for cyclic polyamine. For the case of polyamines comprising rings, a Y' unit of the formula



serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula



therefore comprising no Z terminal unit and having the formula



wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula

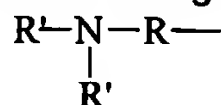


that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 2 to 700, preferably 4 to 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

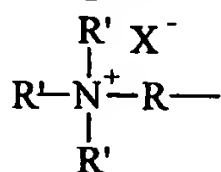
Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, Y' or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units or Y' units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

Modified primary amine moieties are defined as V "terminal" units having one of three forms:

- a) simple substituted units having the structure:

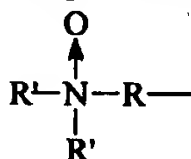


- b) quaternized units having the structure:



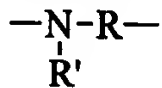
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

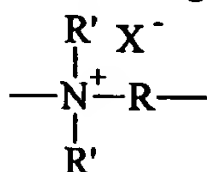


Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

- a) simple substituted units having the structure:

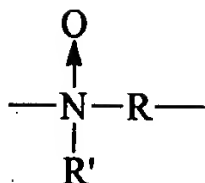


- b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

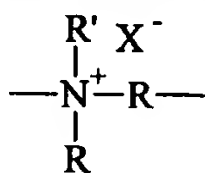


Other modified secondary amine moieties are defined as Y' units having one of three forms:

- a) simple substituted units having the structure:

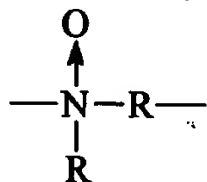


- b) quaternized units having the structure:



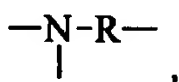
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

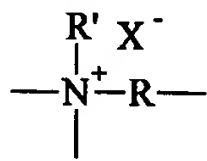


Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

- a) unmodified units having the structure:

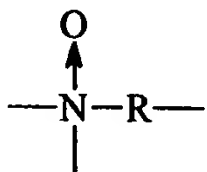


- b) quaternized units having the structure:



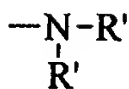
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

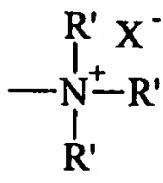


Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

- a) simple substituted units having the structure:

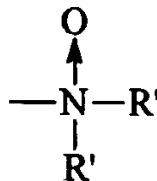


b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

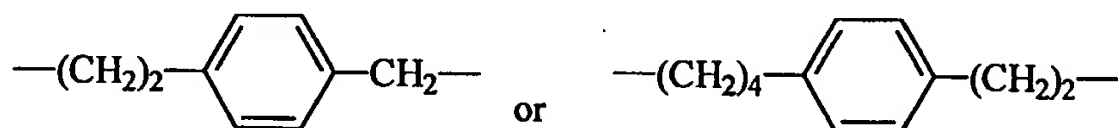


When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for R'. For example, a primary amine unit comprising one R' unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula (HOCH₂CH₂)HN-.

For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure -NH₂. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the R' units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore R' cannot be a hydrogen.

The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C₄-C₁₂ dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected

to the polyamine backbone nitrogens; C8-C12 dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula



although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C2-C12 alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise - (R1O)xR5(OR1)x-, -CH2CH(OR2)CH2O)z(R1O)yR1(OCH2CH(OR2)CH2)w-, -CH2CH(OR2)CH2-, -(R1O)xR1-, and mixtures thereof. Preferred R units are selected from the group consisting of C2-C12 alkylene, C3-C12 hydroxyalkylene, C4-C12 dihydroxyalkylene, C8-C12 dialkylarylene, -(R1O)xR1-, -CH2CH(OR2)CH2-, -(CH2CH(OH)CH2O)z(R1O)yR1(OCH2CH-(OH)CH2)w-, -(R1O)xR5(OR1)x-, more preferred R units are C2-C12 alkylene, C3-C12 hydroxy-alkylene, C4-C12 dihydroxyalkylene, -(R1O)xR1-, -(R1O)xR5(OR1)x-, -(CH2CH(OH)CH2O)z(R1O)yR1(OCH2CH-(OH)CH2)w-, and mixtures thereof, even more preferred R units are C2-C12 alkylene, C3 hydroxyalkylene, and mixtures thereof, most preferred are C2-C6 alkylene. The most preferred backbones of the present invention comprise at least 50% R units that are ethylene.

R1 units are C2-C6 alkylene, and mixtures thereof, preferably ethylene.

R2 is hydrogen, and $-(R1O)_xB$, preferably hydrogen.

R3 is C1-C18 alkyl, C7-C12 arylalkylene, C7-C12 alkyl substituted aryl, C6-C12 aryl, and mixtures thereof, preferably C1-C12 alkyl, C7-C12 arylalkylene, more preferably C1-C12 alkyl, most preferably methyl. R3 units serve as part of R' units described herein below.

R4 is C1-C12 alkylene, C4-C12 alkenylene, C8-C12 arylalkylene, C6-C10 arylene, preferably C1-C10 alkylene, C8-C12 arylalkylene, more preferably C2-C8 alkylene, most preferably ethylene or butylene.

R5 is C1-C12 alkylene, C3-C12 hydroxyalkylene, C4-C12 dihydroxyalkylene, C8-C12 dialkylarylene, -C(O)-, -C(O)NHR6NHC(O)-, -C(O)(R4)rC(O)-, -

R1(OR1)-, -CH₂CH(OH)CH₂O(R1O)_yR1OCH₂CH(OH)CH₂-, -C(O)(R4)_rC(O)-, -CH₂CH(OH)CH₂-, R5 is preferably ethylene, -C(O)-, -C(O)NHR₆NHC(O)-, -R1(OR1)-, -CH₂CH(OH)CH₂-, -CH₂CH(OH)CH₂O(R1O)_yR1OCH₂CH(OH)CH₂-, more preferably -CH₂CH(OH)CH₂-.

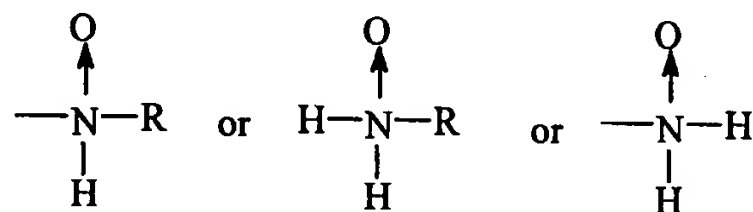
R6 is C₂-C₁₂ alkylene or C₆-C₁₂ arylene.

The preferred "oxy" R units are further defined in terms of the R₁, R₂, and R₅ units. Preferred "oxy" R units comprise the preferred R₁, R₂, and R₅ units. The preferred polyamines of the present invention comprise at least 50% R₁ units that are ethylene. Preferred R₁, R₂, and R₅ units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

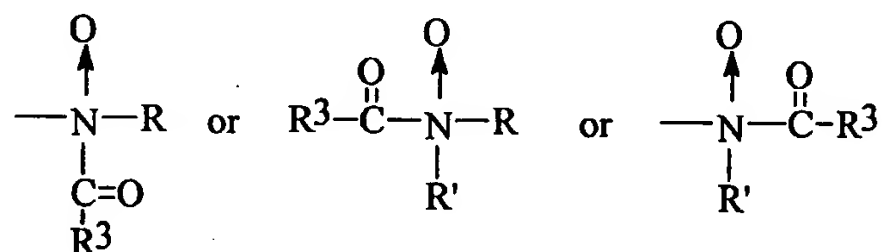
- i) Substituting more preferred R₅ into -(CH₂CH₂O)_xR₅(OCH₂CH₂)_x- yields -(CH₂CH₂O)_xCH₂CHOHCH₂(OCH₂CH₂)_x-.
- ii) Substituting preferred R₁ and R₂ into -(CH₂CH(OR₂)CH₂O)_z(R1O)_yR1O(CH₂CH(OR₂)CH₂)_w- yields -(CH₂CH(OH)CH₂O)_z(CH₂CH₂O)_yCH₂CH₂O(CH₂CH(OH)CH₂)_w-.
- iii) Substituting preferred R₂ into -CH₂CH(OR₂)CH₂- yields -CH₂CH(OH)CH₂-.

R' units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, -(CH₂)_pCO₂M, -(CH₂)_qSO₃M, -CH(CH₂CO₂M)CO₂M, -(CH₂)_pPO₃M, -(R1O)_mB, -C(O)R₃, preferably hydrogen, C₂-C₂₂ hydroxyalkylene, benzyl, C₁-C₂₂ alkylene, -(R1O)_mB, -C(O)R₃, -(CH₂)_pCO₂M, -(CH₂)_qSO₃M, -CH(CH₂CO₂M)CO₂M, more preferably C₁-C₂₂ alkylene, -(R1O)_xB, -C(O)R₃, -(CH₂)_pCO₂M, -(CH₂)_qSO₃M, -CH(CH₂CO₂M)CO₂M, most preferably C₁-C₂₂ alkylene, -(R1O)_xB, and -C(O)R₃. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing R'. A most preferred R' unit is (R1O)_xB.

R' units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



Additionally, R' units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the R' unit -C(O)R³ moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure



or combinations thereof.

B is hydrogen, C1-C6 alkyl, -(CH₂)_qSO₃M, -(CH₂)_pCO₂M, -(CH₂)_q-(CHSO₃M)CH₂SO₃M, -(CH₂)_q(CHSO₂M)CH₂SO₃M, -(CH₂)_pPO₃M, -PO₃M, preferably hydrogen, -(CH₂)_qSO₃M, -(CH₂)_q(CHSO₃M)CH₂SO₃M, -(CH₂)_q-(CHSO₂M)CH₂SO₃M, more preferably hydrogen or -(CH₂)_qSO₃M.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies -(CH₂)_pCO₂M, and -(CH₂)_qSO₃M, thereby resulting in -(CH₂)_pCO₂Na, and -(CH₂)_qSO₃Na moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a -(CH₂)_pPO₃M moiety substituted with sodium atoms has the formula -(CH₂)_pPO₃Na₃. Divalent cations such as calcium (Ca²⁺) or magnesium (Mg²⁺) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

X is a water soluble anion such as chlorine (Cl⁻), bromine (Br⁻) and iodine (I⁻) or X can be any negatively charged radical such as sulfate (SO₄²⁻) and methosulfate (CH₃SO₃⁻).

The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; m has

the value from 2 to 700, preferably from 4 to 400, n has the value from 0 to 350, preferably from 0 to 200; $m + n$ has the value of at least 5.

Preferably x has a value lying in the range of from 1 to 20, preferably from 1 to 10.

The preferred polyamines of the present invention comprise polyamine backbones wherein less than 50% of the R groups comprise "oxy" R units, preferably less than 20%, more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

The most preferred polyamines which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C2-C12 alkylene, preferred is C2-C3 alkylene, most preferred is ethylene.

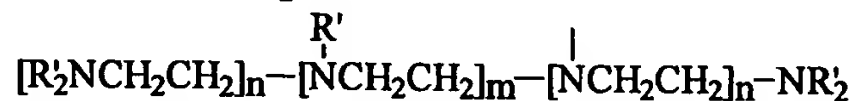
The polyamines of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone.

Preferred polyamines of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneimines (PAI's), preferably polyethyleneimines (PEI's), or PEI's connected by moieties having longer R units than the parent PAI's or PEI's.

Preferred amine polymer backbones comprise R units that are C2 alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



wherein R', m and n are the same as defined herein above. Preferred PEI's will have a molecular weight greater than 200 daltons.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

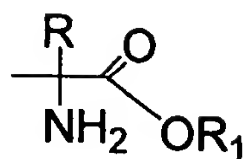
Preferred polyamines are polyethyleneimines commercially available under the tradename Lupasol like Lupasol FG (MW 800), G20wfv (MW 1300), PR8515 (MW 2000), WF (MW 25000), FC (MW 800), G20 (MW 1300), G35 (MW 1200), G100 (MW 2000), HF (MW 25000), P (MW 750000), PS (MW 750000), SK (MW 2000000), SNA (MW 1000000).

Still other polyamine suitable for use in the present invention are poly[oxy(methyl-1,2-ethanediyl)], α -(2-aminomethylethyl)- ω -(2-aminomethyl-ethoxy)- (= C.A.S No. 9046-10-0); poly[oxy(methyl-1,2-ethanediyl)], α -hydro-)- ω -(2-aminomethylethoxy)-, ether with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (= C.A.S. No. 39423-51-3); commercially available under the tradename Jeffamines T-403, D-230, D-400, D-2000; 2,2',2"-triaminotriethylamine; 2,2'-diamino-diethylamine; 3,3'-diamino-dipropylamine, 1,3 bis aminoethyl-cyclohexane commercially available from Mitsibushi and the C12 Sternamines commercially available from Clariant like the C12 Sternamin(propylenamine)_n with n=3/4, and mixtures thereof.

3-Amino acids and derivatives

Still other suitable compounds for use in the present invention are amino acids and their derivatives, especially ester and amide derivatives. More preferred compounds are those providing enhanced surface substantivity due to its structural feature. For clarification, the term amino acids and derivatives does not encompass polymeric compounds.

Suitable amino acids have the following functionality of formula:



Wherein $R_1 = \text{H}$, R^* or $(L)\text{-}R^*$ and R is the amino acid side group, generally referred to as the "R group" such as in "Principles of Biochemistry" by Lehninger et al., 1997, Second Edition, Worth, pp114-116.

Preferred amino acids for use herein are selected tyrosine, tryptophane, lysine, glutamic acid, glutamine, aspartic acid, arginine, asparagine, phenylalanine, proline, glycine, serine, histidine, threonine, methionine, and mixture thereof, most preferably selected from tyrosine, tryptophane, and mixture thereof.

Still other preferred compound are the amino acid derivatives selected from tyrosine ethylate, glycine methylate, tryptophane ethylate, and mixture thereof.

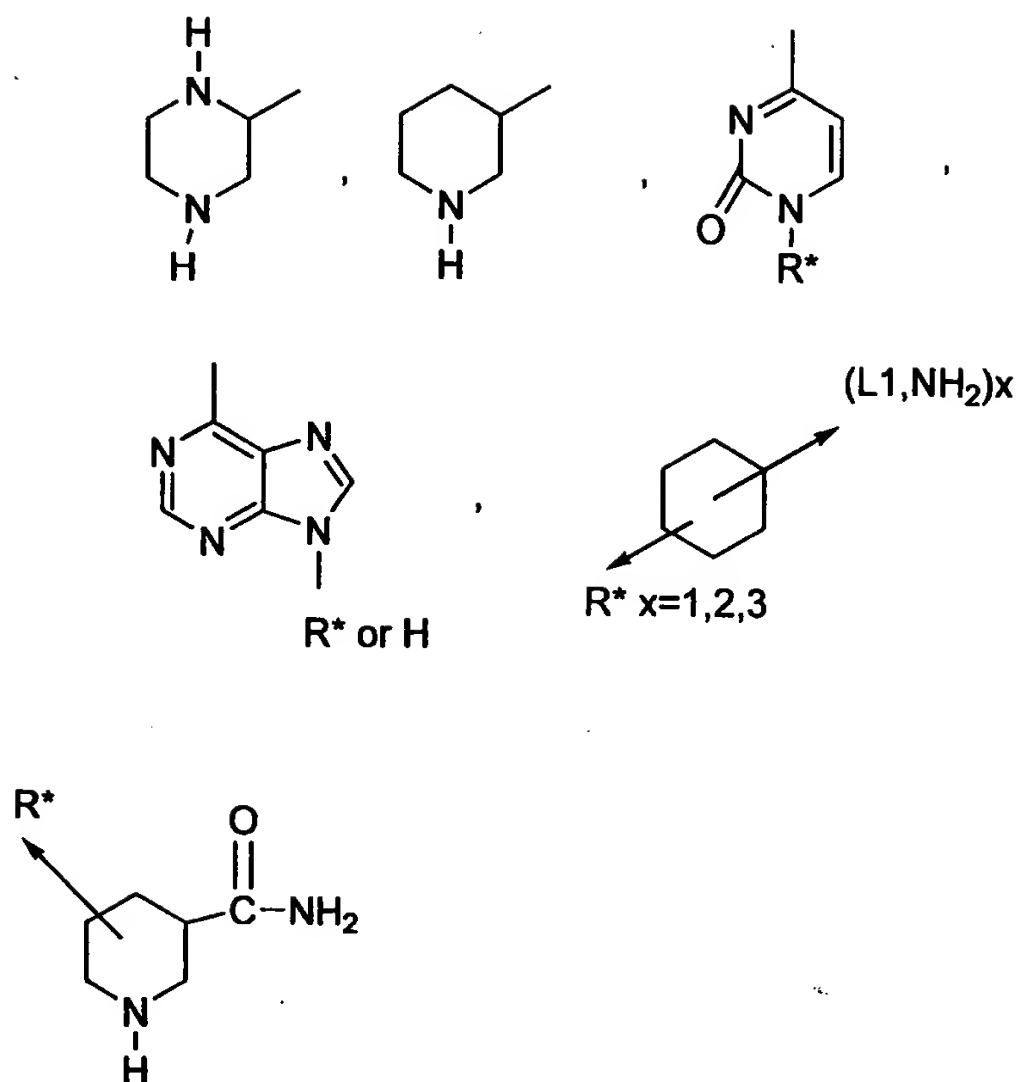
4-Substituted amines and amides

For clarification, the term substituted amines and amides does not encompass polymeric compounds. Substituted amine and amide compounds suitable for use herein have the following general formula:

$\text{NH}_2\text{-L-}R^{**}$, in which L is -CO- in case of an amide.

Other optional linker group may be as defined under R^* .

R^{**} is as defined herein before under R^* with the proviso that it contains at least 6 carbon atoms and/or N atoms and/or cyclohexyl-, piperidine, piperazine, and other heterocyclic groups like:



Optionally, H in NH can be substituted by R*.

Preferred substituted amines and amides for use herein are selected from nipecotamide, N-coco-1,3-propenediamine; N-oley-1,3-propenediamine; N-(tallow alkyl)-1,3-propenediamine; 1,4-diamino cyclohexane; 1,2-diamino-cyclohexane; 1,12-diaminododecane, and mixtures thereof.

5-Glucamines

Still a further preferred class of amine compounds is the class of glucamines of general structure:

$\text{NH}_2\text{-CH}_2\text{-(CH(OH))}_x\text{-CH}_2\text{OH}$, wherein one or several OH-function can be substituted, preferably by -OR^* , and wherein x is an integer of value 3 or 4. R* can be linked to the OH groups either directly or via linker unit as mentioned herein before under L.

For clarification, the term glucamine does not encompass polymeric compounds.

Preferred compound of this class are selected from 2,3,4,5,6-pentamethoxy-glucamine; 6-acetylglucamine, glucamine, and mixture thereof.

6-Dendrimers

Another further class of amine compounds is the class of dendrimers. Suitable dendrimers carry free primary amine groups at the periphery of the spherical molecules, that can be reacted with (perfume) aldehydes or ketones to form the desired amine reaction product (perfume component) of the invention.

By dendrimers it is understood that the molecule is built up from a core molecule as described e.g. in WO 96/02588, in Synthesis, Feb. 1978, p. 155-158 or in Encyclopedia of Polymer Science & Engineering, 2nd ed., Hedstrand et al., in particular pages 46-91. The core is typically connected to multifunctional components to build up the "generations". For the purpose of the present invention, the nature of the inner generations is not critical. They can be based on e.g. polyamidoamines, polyamidoalcohols, polyethers, polyamides, polyethylenimines, etc. Important for the purpose of the present invention is that the outer generation(s) contain accessible primary amino functions.

Also suitable are the glyco dendrimers as described in e.g. Nachrichten aus Chemie 11 (1996), p. 1073-1079 and in WO 97/48711 provided that free primary amine groups are present at the surface of these molecules.

Preferred compounds are the polyethylenimine and/or polypropylenimine dendrimers, the commercially available Starburst[®] polyamidoamines (PAMAM) dendrimers, generation G0-G10 from Dendritech and the dendrimers Astromols[®], generation 1-5 from DSM being DiAminoButane PolyAmine DAB (PA)_x dendrimers with $x = 2^n \times 4$ and n being generally comprised between 0 and 4.

7-Amino-substituted mono-, di-, oligo-, poly-saccharides

Also suitable for the purpose of the present invention are specific amino-substituted mono-, di-, oligo-, poly-saccharides.

For the amino-substituted mono-saccharide of the present invention, it is necessary that the hemi-acetal and/or hemi-ketal functionality is blocked via a

suitable substituent to provide sufficient stability for the intended application. As indicated here above, glucoseamine is not a suitable amine. However, if the hemi-acetal OH function is substituted by R*, said monosaccharide becomes suitable for the purpose of the present invention. The amino group can be in position 2 to 5 or 6 depending on the type of monosaccharide and is preferably in C2, C5 or C6 position. Suitable amino-substituted mono-saccharides are :

- C5 aldosen/ketosen : ribose, arabinose, xylose, lyxose, ribulose, xylulose;
- C6 aldosen/ketosen : allose, altrose, glucose, mannose, gulose, idose, galactose, talose, fructose, sorbose, tagatose, psicose.

For amino-substituted di-saccharides with non-substituted aldose or ketose groups, the free OH-group needs to be substituted by R*, e.g. in lactose and maltose, whereas in sucrose there is no free acetal/ketal OH group. Optionally, more than one OH group can be substituted by R*. Suitable amino-substituted di-saccharides are amino substituted lactose, maltose, sucrose, cellobiose and trehalose.

Suitable amino-substituted oligo-, poly-saccharides are amino-substituted starch, cyclodextrin, dextran, glycogen, cellulose, mannan, guaran, levan, alternan glucose, mannose, galactose, fructose, lactose, maltose, sucrose, cellobiose, cyclodextrin, chitosan, and/or mixtures thereof. The molecules need to carry at least 1, preferably several, amino groups. Chitosan does not require additional amino substitution.

Also suitable for coupling carboxyl- or aldehyde-containing compounds are the following functionalised oligo-, poly-saccharides & glycans commercially available from the company Carbomer. Please find in brackets the reference number from Carbomer :

Amino alginate (5,00002), Diamino alginate (5,00003), Hexanediamine alginate (5,00004 - 5,00006 - 5,00008), dodecanediamine alginate (5,00005 - 5,00007 - 5,00009), 6-amino-6-deoxy cellulose (5,00020), O-ethylamine cellulose (5,00022), O-methylamine cellulose (5,00023), 3-amino-3-deoxy cellulose (5,00024), 2-amino-2 deoxy cellulose (5,00025), 2,3-diamino-2,3-dideoxy cellulose (5,00026), 6-[N-(1,6-hexanediamine)]-6-deoxy cellulose (5,00027), 6-[N-(1, 12-dodecanediamine)]-6-deoxy cellulose (5,00028), O-[methyl-(N-1,6-

hexanediamine)] cellulose (5,00029), O-[methyl-(N-1,12-dodecanediamine)] cellulose (5,00030), 2,3-di-[N-(1,12-dodecanediamine)] cellulose (5,00031), 2,3-diamino-2,3-deoxy alpha-cyclodextrin (5,00050), 2,3-diamino-2,3-deoxy beta-cyclodextrin (5,00051), 2,3-diamino-2,3-deoxy gamma-cyclodextrin (5,00052), 6-amino-6-deoxy alpha-cyclodextrin (5,00053), 6-amino-6-deoxy beta-cyclodextrin (5,00054), O-ethyleamino beta-cyclodextrin (5,00055), 6[N-(1,6-hexanediamino)-6-deoxy alpha cyclodextrin (5,00056), 6[N-(1,6-hexanediamino)-6-deoxy beta cyclodextrin (5,00057), Amino dextran (5,00060), N-[di-(1,6-hexanediamine)] dextran (5,00061), N-[di-(1,12-dodecanediamine)] dextran (5,00062), 6-amino-6-deoxy-alpha-D-galactosyl-guaran (5,00070), O-ethylamino guaran (5,00071), Diamino guaran (5,00072), 6-amino-6-deoxy-starch (5,00080), O-ethylamino starch (5,00081), 2,3-diamine-2,3-dideoxy starch (5,00082), N-[6-(1,6-hexanediamine)]-6-deoxy starch (5,00083), N-[6-(1,12-dodecanediamine)]-6-deoxy starch (5,00084) and 2,3-di-[N(1,6-hexanediamine)]-2,3-dideoxy starch (5,00085)

Furthermore, with the use of some of the above compound comprising at least one primary and/or secondary amine group like the polyamine, the resulting amine reaction product will beneficially provide fabric appearance benefits, in particular color care and protection against fabric wear. Indeed, the appearance of fabrics, e.g., clothing, bedding, household fabrics like table linens is one of the area of concern to consumers. Indeed, upon typical consumer's uses of the fabrics such as wearing, washing, rinsing and/or tumble-drying of fabrics, a loss in the fabric appearance; which can be at least partly due to loss of color fidelity and color definition, is observed. Such a problem of color loss is even more acute after multiwash cycles. It has been found that the compositions of the present invention provide improved fabric appearance and protection against fabric wear and improved color care to laundered fabrics, especially after multiwash cycles.

Therefore, the compositions of the present invention can provide simultaneously fabric care and long lasting perfume benefits.

B-Perfume

Preferably, for the above mentioned compounds, by perfume ketone or active aldehyde, it is meant any chain containing at least 1 carbon atom, preferably at least 5 carbon atoms.

A typical disclosure of suitable ketone and/or aldehydes, traditionally used in perfumery, can be found in "perfume and Flavor Chemicals", Vol. I and II, S. Arctander, Allured Publishing, 1994, ISBN 0-931710-35-5.

Perfume ketones components include components having odoriferous properties.

Preferably, for the above mentioned compounds, the perfume ketone is selected for its odor character from buccoxime; iso jasmone; methyl beta naphthyl ketone; musk indanone; tonalid/musk plus; Alpha-Damascone, Beta-Damascone, Delta-Damascone, Iso-Damascone, Damasconone, Damarose, Methyl-Dihydrojasmonate, Menthone, Carvone, Camphor, Fenchone, Alpha-Ionone, Beta-Ionone, Gamma-Methyl so-called Ionone, Fleuramone, Dihydrojasmone, Cis-Jasmone, Iso-E-Super, Methyl- Cedrenyl-ketone or Methyl-Cedrylone, Acetophenone, Methyl-Acetophenone, Para-Methoxy-Acetophenone, Methyl-Beta-Naphtyl-Ketone, Benzyl-Acetone, Benzophenone, Para-Hydroxy-Phenyl-Butanone, Celery Ketone or Livescone, 6-Isopropyldecahydro-2-naphtone, Dimethyl-Octenone, Freskomenthe, 4-(1-Ethoxyvinyl)-3,3,5,5,-tetramethyl-Cyclohexanone, Methyl-Heptenone, 2-(2-(4-Methyl-3-cyclohexen-1-yl)propyl)-cyclopentanone, 1-(p-Menthen-6(2)-yl)-1-propanone, 4-(4-Hydroxy-3-methoxyphenyl)-2-butanone, 2-Acetyl-3,3-Dimethyl-Norbornane, 6,7-Dihydro-1,1,2,3,3-Pentamethyl-4(5H)-Indanone, 4-Damascol, Dulcinyll or Cassione, Gelsone, Hexalon, Isocyclemonone E, Methyl Cyclocitrone, Methyl-Lavender-Ketone, Orivon, Para-tertiary-Butyl-Cyclohexanone, Verdone, Delphone, Muscone, Neobutenone, Plicatone, Veloutone, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Tetrameran.

Preferably, for the above mentioned compounds, the preferred ketones are selected from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-Ionone, Iso-E-Super, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damasconone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof.

Perfume aldehyde components include components having odoriferous properties.

Preferably, for the above mentioned compounds, the perfume aldehyde is selected for its odor character from adoxal; anisic aldehyde; cymal; ethyl vanillin; florhydral; helional; heliotropin; hydroxycitronellal; koavone; lauric aldehyde; lyral; methyl nonyl acetaldehyde; P. T. buccinal; phenyl acetaldehyde; undecylenic aldehyde; vanillin; 2,6,10-trimethyl-9-undecenal, 3-dodecen-1-al, alpha-n-amylic cinnamic aldehyde, 4-methoxybenzaldehyde, benzaldehyde, 3-(4-tert butylphenyl)-propanal, 2-methyl-3-(para-methoxyphenyl)propanal, 2-methyl-4-(2,6,6-trimethyl-2(1)-cyclohexen-1-yl)butanal, 3-phenyl-2-propenal, cis-/trans-3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-6-octen-1-al, [(3,7-dimethyl-6-octenyl)oxy] acetaldehyde, 4-isopropylbenzaldehyde, 1,2,3,4,5,6,7,8-octahydro-8,8-dimethyl-2-naphthaldehyde, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, 2-methyl-3-(isopropylphenyl)propanal, 1-decanal; decyl aldehyde, 2,6-dimethyl-5-heptenal, 4-(tricyclo[5.2.1.0(2,6)]-decylidene-8)-butanal, octahydro-4,7-methano-1H-indenecarboxaldehyde, 3-ethoxy-4-hydroxybenzaldehyde, para-ethyl-alpha, alpha-dimethyl hydrocinnamaldehyde, alpha-methyl-3,4-(methylenedioxy)-hydrocinnamaldehyde, 3,4-methylenedioxybenzaldehyde, alpha-n-hexyl cinnamic aldehyde, m-cymene-7-carboxaldehyde, alpha-methyl phenyl acetaldehyde, 7-hydroxy-3,7-dimethyloctanal, Undecenal, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde, 4-(3)-(4-methyl-3-pentenyl)-3-cyclohexene-carboxaldehyde, 1-dodecanal, 2,4-dimethylcyclohexene-3-carboxaldehyde, 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde, 7-methoxy-3,7-dimethyloctan-1-al, 2-methyl undecanal, 2-methyl decanal, 1-nonanal, 1-octanal, 2,6,10-trimethyl-5,9-undecadienal, 2-methyl-3-(4-tertbutyl)propanal, dihydrocinnamic aldehyde, 1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carboxaldehyde, 5 or 6 methoxyhexahydro-4,7-methanoindan-1 or 2- carboxaldehyde, 3,7-dimethyloctan-1-al, 1-undecanal, 10-undecen-1-al, 4-hydroxy-3-methoxy benzaldehyde, 1-methyl-3-(4-methylpentyl)-3-cyclohexenecarboxaldehyde, 7-hydroxy-3,7-dimethyl-octanal, trans-4-decenal, 2,6-nonadienal, para-tolylacetaldehyde; 4-methylphenylacetaldehyde, 2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butanal, ortho-methoxycinnamic aldehyde, 3,5,6-trimethyl-3-cyclohexene carboxaldehyde, 3,7-dimethyl-2-methylene-6-octenal, phenoxyacetaldehyde, 5,9-dimethyl-4,8-decadienal, peony

aldehyde (6,10-dimethyl-3-oxa-5,9-undecadien-1-al), hexahydro-4,7-methanoindan-1-carbox-aldehyde, 2-methyl octanal, alpha-methyl-4-(1-methyl ethyl) benzene acetaldehyde, 6,6-dimethyl-2-norpinene-2-propionaldehyde, para methyl phenoxy acetaldehyde, 2-methyl-3-phenyl-2-propen-1-al, 3,5,5-trimethyl hexanal, Hexahydro-8,8-dimethyl-2-naphthaldehyde, 3-propyl-bicyclo[2.2.1]-hept-5-ene-2-carbaldehyde, 9-decenal, 3-methyl-5-phenyl-1-pentanal, methylnonyl acetaldehyde, hexanal, trans-2-hexenal, 1-p-menthene-q-carboxaldehyde and mixtures thereof.

Most preferred aldehydes are selected from 1-decanal, benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadienal; alpha-n-amyl cinnamic aldehyde, alpha-n-hexyl cinnamic aldehyde, P.T. Bucinal, lylal, cymal, methyl nonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof.

In the above list of perfume ingredients, some are commercial names conventionally known to one skilled in the art, and also includes isomers. Such isomers are also suitable for use in the present invention.

In another embodiment, especially suitable for the purpose of the present invention are the perfume compounds, preferably the perfume ketones or active aldehydes, characterised by having a low Odor Detection Threshold. Such Odor Detection Threshold (ODT) should be lower than or equal to 1ppm, preferably lower than or equal to 10ppb - measured at controlled Gas Chromatography (GC) conditions such as described here below. This parameter refers to the value commonly used in the perfumery arts and which is the lowest concentration at which significant detection takes place that some odorous material is present. Please refer for example in "Compilation of Odor and Taste Threshold Value Data (ASTM DS 48 A)", edited by F. A. Fazzalari, International Business Machines, Hopwell Junction, NY and in Calkin et al., Perfumery, Practice and Principles, John Willey & Sons, Inc., page 243 et seq (1994). For the purpose of the present invention, the Odor Detection Threshold is measured according to the following method :

The gas chromatograph is characterized to determine the exact volume of material injected by the syringe, the precise split ratio, and the hydrocarbon

response using a hydrocarbon standard of known concentration and chain-length distribution. The air flow rate is accurately measured and, assuming the duration of a human inhalation to last 0.02 minutes, the sampled volume is calculated. Since the precise concentration at the detector at any point in time is known, the mass per volume inhaled is known and hence the concentration of material. To determine the ODT of a perfume material, solutions are delivered to the sniff port at the back-calculated concentration. A panelist sniffs the GC effluent and identifies the retention time when odor is noticed. The average over all panelists determines the threshold of noticeability. The necessary amount of analyte is injected onto the column to achieve a certain concentration, such as 10 ppb, at the detector. Typical gas chromatograph parameters for determining odor detection thresholds are listed below.

GC: 5890 Series II with FID detector

7673 Autosampler

Column: J&W Scientific DB-1

Length 30 meters ID 0.25 mm film thickness 1 micron

Method:

Split Injection: 17/1 split ratio

Autosampler: 1.13 microliters per injection

Column Flow: 1.10 mL/minute

Air Flow: 345 mL/minute

Inlet Temp. 245°C

Detector Temp. 285°C

Temperature Information

Initial Temperature: 50°C

Rate: 5C/minute

Final Temperature: 280°C

Final Time: 6 minutes

Leading assumptions: 0.02 minutes per sniff

GC air adds to sample dilution

Examples of such preferred perfume components are those selected from : 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde, 1-(2,6,6-trimethyl-2-cyclohexan-1-yl)-2-buten-1-one and/or para-methoxy-acetophenone. Even more preferred are the following compounds having an ODT ≤ 10 ppb measured with the method described above : undecylenic aldehyde, undecalactone gamma,

heliotropin, dodecalactone gamma, p-anisic aldehyde, para hydroxy-phenyl-butanone, cymal, benzyl acetone, ionone alpha, p.t.bucinal, damascenone, ionone beta and methyl-nonyl ketone.

Typically the level of active is of from 10 to 90%, preferably from 30 to 85%, more preferably from 45 to 80% by weight of the amine reaction product.

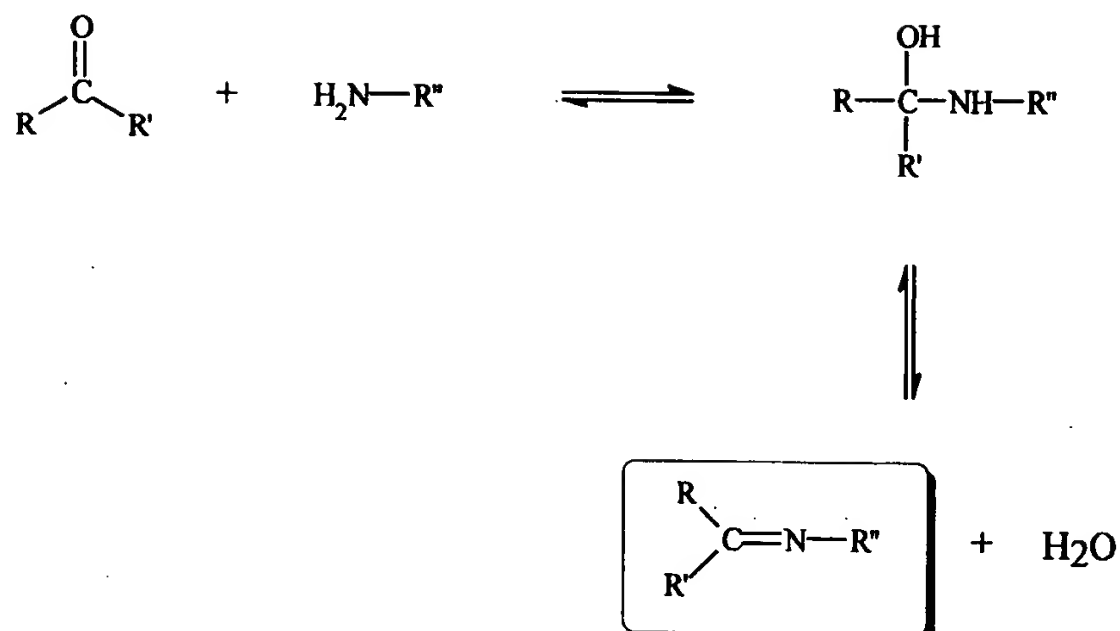
Preferred amine reaction products are those resulting from the reaction of poethyleneimine polymer like Lupasol polymers, with one or more of the following Alpha Damascone, Delta Damascone, Carvone, Hedione, Florhydral, Lilial, Heliotropine, Gamma-Methyl-Ionone and 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde. Still other preferred amine reaction products are those resulting from the reaction of Atramol Dendrimers with Carvone as well as those resulting from the reaction of ethyl-4-amino benzoate with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde.

Most preferred amine reaction products are those from the reaction of Lupasol HF with Delta Damascone; LupasolG35 with Alpha Damascone; LupasolG100 with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, ethyl-4-amino benzoate with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde.

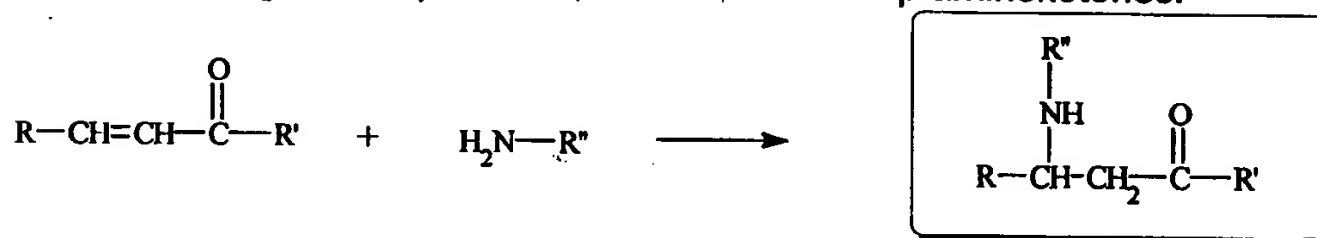
Process

Preparation of the component is made as follows in the Synthesis Examples. In general, the nitrogen analogs of ketones and aldehydes are called azomethines, Schiff bases or the more preferred name imines. These imines can easily be prepared by condensation of primary amines and carbonyl compounds by elimination of water.

A typical reaction profile is as follows:



α,β -Unsaturated ketones do not only condense with amines to form imines, but can also undergo a competitive 1,4-addition to form β -aminoketones.



By means of this simple method, compound and composition containing said compounds are made which achieve a delayed release of the active ingredient.

As can be observed, the perfume ingredient is typically present in equimolar amount to the amine function so as to enable the reaction to take place and provide the resulting amine reaction product. Of course, higher amount are not excluded and even preferred when the amine compound comprises more than one amine function. When the amine compound has more than one free primary and/or secondary amine group, several different perfume raw materials can be linked to the amine compound.

Mechanism of release

By the present invention, a delayed release of a perfume ingredient, i.e. ketone or aldehyde is obtained. Not to be bound by theory, the release is believed to occur by the following mechanisms:

For imine compounds, the perfume components are released upon breaking down of the imine bond, leading to the release of the perfume component and of the primary amine compound. This can be achieved by either hydrolysis, photochemical cleavage, oxidative cleavage, or enzymatic cleavage.

For β -aminoketone compounds, treatment with air moisture and/or water successfully releases the perfume component and the amine compound. However, other means of release are not excluded like hydrolysis, photochemical cleavage, oxidative cleavage, or enzymatic cleavage.

Still other means of release for imine as well as β -aminoketone compounds can be considered such as by the steaming step of ironing the treated fabric, tumble-drying, and/or wearing.

Laundry and cleaning compositions

The present invention include both laundry and cleaning compositions which are typically used for laundering fabrics and cleaning hard surfaces such as dishware, floors, bathrooms, toilet, kitchen and other surfaces in need of a delayed release of perfume ketone and/or aldehyde. Accordingly, by laundry and cleaning compositions, these are to be understood to include not only detergent compositions which provide fabric cleaning benefits, but also compositions such as hard surface cleaning which provide hard surface cleaning benefit.

Preferred are those laundry compositions which result in contacting the compound of the invention with fabric.

Preferably, the amine reaction product(s) which is incorporated into such laundry and cleaning compositions provides a dry surface Odor Index of more than 5 preferably at least 10.

By Dry Surface Odor Index, it is meant that the amine reaction product(s) provides a Delta of more than 5, wherein Delta is the difference between the Odor Index of the dry surface treated with amine reaction product(s) and the Odor Index of the dry surface treated with only the perfume raw material.

Measurement method of Dry Surface Odor Index:

For the above Dry Surface Odor Index, the amine reaction product suitable for use in the present invention needs to fulfill at least one of the following two tests. Preferred amine reaction product suitable for use in the present invention fulfill both test.

1)-For fabric surface**Product preparation:**

The amine reaction product is added to the unperfumed product base.

The unperfumed product base, wherein the abbreviations are as defined herein after for the examples, is as follows:

| Composition | % by weight |
|--------------------------------|-------------|
| LAS | 16 |
| NaSKS-6 | 6 |
| PB1 | 8 |
| TAED | 2.4 |
| Carbonate | 1 |
| Sodium Carbonate | 1 |
| HEDP | 0.4 |
| SRP1 | 0.2 |
| Photobleach | 0.013 |
| Citric acid | 1.0 |
| Protease | 0.3 |
| Lipase | 0.1 |
| Cellulase | 0.1 |
| Amylase | 0.3 |
| Zeolite | 3.0 |
| TFAA | 3.0 |
| QAS1 | 2.5 |
| Silicone antifoam | 1.0 |
| Misc/minors to balance to 100% | |

Levels of amine reaction product are selected so as to obtain an odor grade on the dry fabric of at least 20. After careful mixing, by shaking the container in case of a liquid, with a spatula in case of a powder, the product is allowed to sit for 24 hrs.

Washing process:

The resulting product is added into the washing machine in the dosage and in the dispenser appropriate for its category. The quantity corresponds to recommended dosages made for the corresponding market products: typically between 70 and 150 g for a detergent powder or liquid via current dosing device like granulette, or arielle. The load is composed of four bath towels (170g) using a Miele W830 washing machine at 40°C short cycle, water input :15°Hardness at a temperature of 10-18°C, and full spin of 1200rpm.

The same process is applied for the corresponding free perfume ingredient in consideration and is used as the reference. Dosages, fabric loads and washing cycles for the reference and the sample are identical.

Drying Process:

Within two hours after the end of the washing cycle, the spinned but still wet fabrics are assessed for their odors using the scale mentioned below. Afterwards, half of the fabric pieces are hung on a line for 24 hr drying, away from any possible contaminations. Unless specified, this drying takes place indoor. Ambient conditions are at temperature between 18-25C and air moisture between 50-80%. The other half is placed in a tumble drier and undergoes a full "very dry" cycle, i.e. in a Miele, Novotronic T430 set on program white-extra dry (full cycle). Tumble dry fabrics are also assessed on the next day. Fabrics are then stored in opened aluminum bags in an odor free room, and assessed again after 7 days.

Odor Evaluations:

Odor is assessed by expert panellist smelling the fabrics. A 0-100 scale is used for all fabric odor gradings. The grading scale is as follows :

- 100 = extremely strong perfume odor
- 75 = very strong perfume odor
- 50 = strong odor

40 = moderate perfume odor
 30 = slight perfume odor
 20 = weak perfume odor
 10 = very weak perfume odor
 0 = no odor

A difference of more than 5 grades after one day and/or 7 days between the amine reaction product and the perfume raw material is statistically significant. A difference of 10 grades or more after one day and/or 7 days represents a step-change. In other words, when a difference of grade of more than 5, preferably at least 10 is observed between the amine reaction product and the perfume raw material, after either 1 day or 7 days or both 1 day and 7 days, it can be concluded that the amine reaction product is suitable for use in the present invention, provided that the amine compound fulfill the Odor Intensity Index.

2)-For hard surface:

Product preparation:

The perfume raw material or blend thereof is added and carefully mixed at 0.255% in the unperfumed Hard Surface Cleaner base.

The unperfumed product base, wherein the abbreviations are as defined herein after for the examples, is as follows:

| Composition for hard surface test | % by weight |
|--|-------------|
| C12-14 EO 21 | 2 |
| C12-14 EO 5 | 2.5 |
| C9-11 EO 5 | 2.5 |
| LAS | 0.8 |
| Na ₂ CO ₃ | 0.2 |
| Citric acid | 0.8 |
| Caustic acid | 0.5 |
| Fatty acid | 0.5 |
| SCS | 1.5 |
| Water & Misc/Minors to balance to 100% | |

After mixing and standing for 24 hrs, the homogeneity of the product is checked. In case of phase separation due to poor solubility of the perfume ingredient(s) an appropriate amount of Sodium p. Cymene Sulfonate or another solubilising agent is added till a homogeneous solution is obtained.

Cleaning process:

Five grams of this solution are evenly applied on the upper side of a ceramic tile (875 square cm, e.g. from Vileroy-Boch). After 1 minute the tile is rinsed with 1 liter of tap water. The tile is then placed in a vertical position for 3 minutes to allow the rinse water to drip off.

Finally, the tile is placed in a clean and aerated perspex box (38 x 40 x 32 cm) with a removable cover that has a sliding-lid (10 x 10 cm) to allow expert evaluators to smell the interior phase of the box.

The odor in the box is evaluated just after placing the tile in it (fresh reading) and after 1, 2 and 6 hours.

Odor Evaluation:

The grading scale is as follows :

- 50 = very strong odor
- 40 = strong odor
- 30 = moderate odor
- 20 = slight odor
- 10 = weak odor
- 0 = no odor

Every test includes a blanc (unperfumed Hard Surface Cleaner) and in the case of testing perfume precursor, so-called amine reaction product the corresponding free perfume ingredient is also included so that the effect of the carrier is adequately measured.

Again as for the Dry surface Odor Index method for fabrics, a difference of more than 5 grades after 1 day and/or 7 days between the amine reaction product and the perfume raw material is statistically significant. A difference of 10 grades or more after 1 day and/or 7 days represents a step-change. In other words, when a difference of grade of more than 5, preferably at least 10 is observed between

the amine reaction product and the perfume raw material, after either 1 day or 7 day or both 1 day and 7 days, it can be concluded that the amine reaction product is suitable for use in the present, provided that the amine compound fulfill the Odor Intensity Index.

The amine reaction product as defined herein before typically is comprised at from 0.0001% to 10%, preferably from 0.001% to 5%, and more preferably from 0.01% to 2%, by weight of the composition. Mixtures of the compounds may also be used herein.

Incorporation of the amine reaction product in the laundry and cleaning compositions can conveniently be carried out, if necessary, by conventional incorporation means, such as by spray-on, encapsulation or agglomeration with starch and/or carbonate, and/or sulfate, and/or clay, e.g. as described in GB1464616, dry addition, or by encapsulation in cyclodextrin. Preferably, the amine reaction product is preformed before incorporation into the laundry and cleaning compositions. In other words, the perfume component and the amine compound are first reacted together to obtain the resulting amine reaction product as defined in the present invention and only once formed incorporated into the laundry and cleaning compositions. By being preformed before the incorporation in fully formulated composition, a better control of the compound being made is obtained. Hence, the interaction with perfume composition which may be present in fully formulated composition is avoided as well as side reaction that could occur. Further, by such means of incorporation, efficient control of the yield and purity of the compound is obtained.

Most preferably, when the laundry and cleaning composition comprises a perfume, the amine reaction product is incorporated in the composition separately from the perfume. By this means, the amine reaction product and its subsequent perfume release is more controlled.

Typically the laundry and cleaning composition comprises a deterative ingredient and further optional ingredients as described hereinafter as optional ingredients.

Deterative ingredients

Non-limiting examples of surfactants useful herein typically at levels from 1% to 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula $\text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3^- \text{M}^+) \text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3^- \text{M}^+) \text{CH}_2\text{CH}_3$ where x and (y + 1) are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially x up to 7 EO ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-18 glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, cationic surfactants and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Fully formulated laundry and cleaning compositions preferably contain, in addition to the hereinbefore described components, one or more of the following ingredients.

Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least 1% builder, preferably from 1% to 80%. Liquid formulations typically comprise from 5% to 50%, more typically 5% to 30%, by weight, of detergent builder. Granular formulations typically comprise from 1% to 80%, more typically from 5% to 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.0:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. 4,664,839. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular

formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

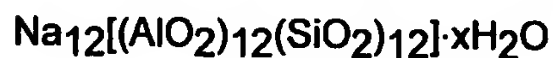
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in DE 2,321,001.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers usually of at least 6, the molar ratio of z to y is in the range from 1.0 to 0, and x is an integer from 0 to 264, and M is a Group IA or IIA element, e.g., Na, K, Mg, Ca with valence n.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from 20 to 30, especially 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. 3,128,287, U.S. 3,635,830. See also "TMS/TDS" builders of U.S. 4,663,071. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, pyromellitic, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in EP 0,200,263.

Other suitable polycarboxylates are disclosed in U.S. 4,144,226 and in U.S. 3,308,067. See also U.S. 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids such as oleic acid and/or its salts, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Bleaching Compounds - Bleaching Agents and Bleach Activators

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from 1% to 30%, more typically from 5% to 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from 0.1% to 60%, more typically from 0.5% to 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents like hypochlorite bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein. When hypochlorite is used, a highly preferred hypochlorite bleaching component is an alkali metal hypochlorite. Although alkali metal hypochlorites are preferred, other hypochlorite compounds may also be used herein and can be selected from calcium and magnesium hypochlorite. A preferred alkali metal hypochlorite for use herein is sodium hypochlorite.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. 4,483,781, U.S. 740,446, EP 0,133,354, and U.S. 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxy caproic acid as described in U.S. 4,634,551.

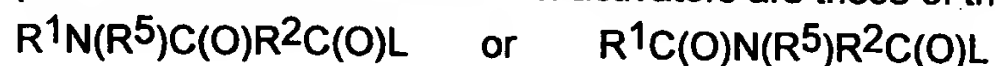
Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from 500 micrometers to 1,000 micrometers, not more than 10% by weight of said particles being smaller than 200 micrometers and not more than 10% by weight of said particles being larger than 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. 4,915,854, and U.S. 4,412,934. The nonanoyloxybenzene sulfonate (NOBS), 3,5,5-trimethyl hexanoyl oxybenzene sulfonate (ISONOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

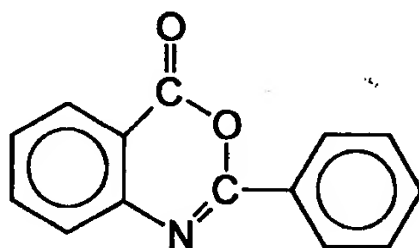
Highly preferred amido-derived bleach activators are those of the formulae:



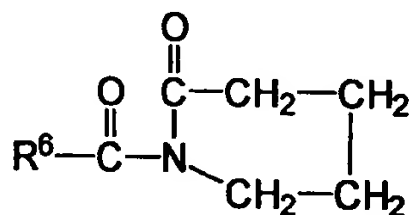
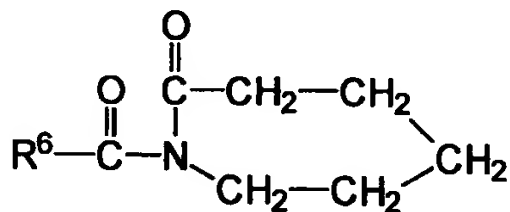
wherein R^1 is an alkyl group containing from 6 to 12 carbon atoms, R^2 is an alkylene containing from 1 to 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from 1 to 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. 4,033,718. If used, detergent compositions will typically contain from 0.025% to 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

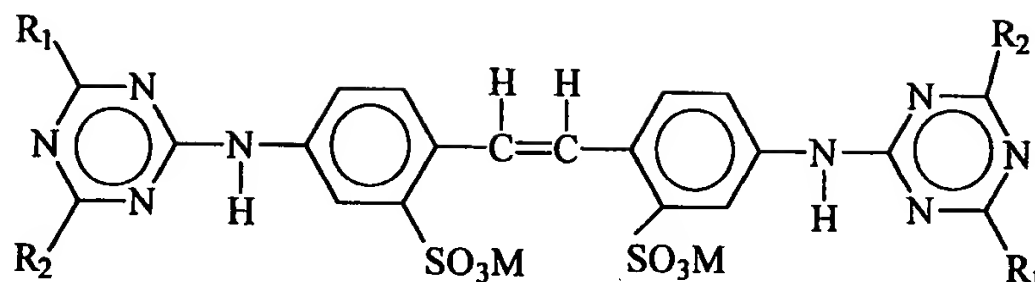
If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well-known in the art and include, for example, the manganese-based catalysts disclosed in U.S. 5,246,621, U.S. 5,244,594; U.S. 5,194,416; U.S. 5,114,606; and EP 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\mu\text{-O})_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{PF}_6)_2$, $\text{Mn}^{\text{III}}_2(\mu\text{-O})_1(\mu\text{-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\mu\text{-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\mu\text{-O})_1(\mu\text{-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_3$, $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})\text{-(OCH}_3)_3(\text{PF}_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following US Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from 0.1 ppm to 700 ppm, more preferably from 1 ppm to 500 ppm, of the catalyst species in the laundry liquor.

Brighteners

The compositions herein can also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from 0.001% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX[®] by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the rinse added compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX[®] by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX[®] by Ciba Geigy Corporation.

Soil Release Agent

In the present invention, an optional soil release agent can be added. Typical levels of incorporation in the composition are from 0% to 10%, preferably from 0.2% to 5%, of a soil release agent. Preferably, such a soil release agent is a polymer.

Soil Release agents are desirably used in fabric softening compositions of the instant invention. Any polymeric soil release agent known to those skilled in the

art can optionally be employed in the compositions of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 3,959,230 Hays, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; U.S. 4,000,093, Nicol, *et al.*; issued December 28, 1976; U.S. Patent 4,702,857 Gosselink, issued October 27, 1987; U.S. 4,968,451, Scheibel *et al.*, issued November 6; U.S. 4,702,857, Gosselink, issued October 27, 1987; U.S. 4,711,730, Gosselink *et al.*, issued December 8, 1987; U.S. 4,721,580, Gosselink, issued January 26, 1988; U.S. 4,877,896, Maldonado *et al.*, issued October 31, 1989; U.S. 4,956,447, Gosselink *et al.*, issued September 11, 1990; U.S. 5,415,807 Gosselink *et al.*, issued May 16, 1995; European Patent Application 0 219 048, published April 22, 1987 by Kud, *et al.*

Further suitable soil release agents are described in U.S. 4,201,824, Violland *et al.*; U.S. 4,240,918 Lagasse *et al.*; U.S. 4,525,524 Tung *et al.*; U.S. 4,579,681, Ruppert *et al.*; U.S. 4,240,918; U.S. 4,787,989; U.S. 4,525,524; EP 279,134 A, 1988, to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N. V., 1974 all incorporated herein by reference.

Commercially available soil release agents include the METOLOSE SM100, METOLOSE SM200 manufactured by Shin-etsu Kagaku Kogyo K.K., SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (Germany), ZELCON 5126 (from Dupont) and MILEASE T (from ICI).

Scum Dispersant

In the present invention, the premix can be combined with an optional scum dispersant, other than the soil release agent, and heated to a temperature at or above the melting point(s) of the components.

The preferred scum dispersants herein are formed by highly ethoxylating hydrophobic materials. The hydrophobic material can be a fatty alcohol, fatty acid, fatty amine, fatty acid amide, amine oxide, quaternary ammonium compound, or the hydrophobic moieties used to form soil release polymers. The preferred scum dispersants are highly ethoxylated, e.g., more than 17, preferably more than 25, more preferably more than 40, moles of ethylene oxide per molecule on the average, with the polyethylene oxide portion being from 76% to 97%, preferably from 81% to 94%, of the total molecular weight.

The level of scum dispersant is sufficient to keep the scum at an acceptable, preferably unnoticeable to the consumer, level under the conditions of use, but not enough to adversely affect softening. For some purposes it is desirable that the scum is nonexistent. Depending on the amount of anionic or nonionic detergent, etc., used in the wash cycle of a typical laundering process, the efficiency of the rinsing steps prior to the introduction of the compositions herein, and the water hardness, the amount of anionic or nonionic detergent surfactant and detergency builder (especially phosphates and zeolites) entrapped in the fabric (laundry) will vary. Normally, the minimum amount of scum dispersant should be used to avoid adversely affecting softening properties. Typically scum dispersion requires at least 2%, preferably at least 4% (at least 6% and preferably at least 10% for maximum scum avoidance) based upon the level of softener active. However, at levels of 10% (relative to the softener material) or more, one risks loss of softening efficacy of the product especially when the fabrics contain high proportions of nonionic surfactant which has been absorbed during the washing operation.

Preferred scum dispersants are: Brij 700®; Varonic U-250®; Genapol T-500®, Genapol T-800®, Plurafac A-79®, and Neodol 25-50®.

Bactericides

Examples of bactericides used in the compositions of this invention include glutaraldehyde, formaldehyde, 2-bromo-2-nitro-propane-1,3-diol sold by Inolex Chemicals, located in Philadelphia, Pennsylvania, under the trade name Bronopol®, and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-

methyl-4-isothiazoline-3-one sold by Rohm and Haas Company under the trade name Kathon 1 to 1,000 ppm by weight of the agent.

Perfume

The present invention can contain any detergent compatible perfume. Suitable perfumes are disclosed in U.S. Pat. 5,500,138, said patent being incorporated herein by reference.

As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

Examples of perfume ingredients useful in the perfumes of the present invention compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpineol; 3,7-dimethyl-*cis*-2,6-octadien-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-*trans*-2,6-octadien-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecenyl propionate; tricyclodecenyl acetate; anisaldehyde; 2-methyl-2-(para-isopropylphenyl)-propionaldehyde; ethyl-3-methyl-3-phenyl glycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-methoxyacetophenone; para-methoxy-alpha-phenylpropene; methyl-2-n-hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl) acetate; beta-naphthol methylether; methyl-beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert-butylcyclohexyl acetate; alpha,alpha-dimethylphenethyl acetate; methylphenylcarbinyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate; cyclic ethyleneglycol diester of tridecandioic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone alpha; ionone beta; petitgrain; methyl cedrylone; 7-acetyl-

1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl; methyl-1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; isohexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate; patchouli; olibanum resinoid; labdanum; vetivert; copaiba balsam; fir balsam; and condensation products of: hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phenyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate.

More examples of perfume components are geraniol; geranyl acetate; linalool; linalyl acetate; tetrahydrolinalool; citronello; citronellyl acetate; dihydromyrcenol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopol; nopyl acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl benzoate; styrallyl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbiny methylphenylcarbiny acetate; isononyl acetate; vetiveryl acetate; vetiverol; 2-methyl-3-(p-tert-butylphenyl)-propanal; 2-methyl-3-(p-isopropylphenyl)-propanal; 3-(p-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde; 4-acetoxy-3-pentyltetrahydropyran; methyl dihydrojasmonate; 2-n-heptylcyclopentanone; 3-methyl-2-pentylcyclopentanone; n-decanal; n-dodecanal; 9-decenol-1; phenoxyethyl isobutyrate; phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethylacetal; geranonitrile; citronellonitrile; cedryl acetal; 3-isocamphylcyclohexanol; cedryl methylether; isolongifolanone; aubepine nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal ionones; methyl ionones; isomethyl ionones; irones; cis-3-hexenol and esters thereof; indane musk fragrances; tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macrolactone musk fragrances; ethylene brassylate.

The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

Suitable solvents, diluents or carriers for perfumes ingredients mentioned above are for examples, ethanol, isopropanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a homogeneous perfume solution.

Perfume can be present at a level of from 0% to 10%, preferably from 0.1% to 5%, and more preferably from 0.2% to 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

Chelating Agents

The compositions and processes herein can optionally employ one or more copper and/or nickel chelating agents ("chelators"). Such water-soluble chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof, all as hereinafter defined. The whiteness and/or brightness of fabrics are substantially improved or restored by such chelating agents and the stability of the materials in the compositions are improved. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetra-amine-hexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

Preferred chelating agents include DETMP, DETPA, NTA, EDDS and mixtures thereof.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the fabric care compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Crystal growth inhibitor component

The compositions of the present invention can further contain a crystal growth inhibitor component, preferably an organodiphosphonic acid component, incorporated preferably at a level of from 0.01% to 5%, more preferably from 0.1% to 2% by weight of the compositions.

By organo diphosphonic acid it is meant herein an organo diphosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrant components.

The organo diphosphonic acid is preferably a C₁-C₄ diphosphonic acid, more preferably a C₂ diphosphonic acid, such as ethylene diphosphonic acid, or most

preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP) and may be present in partially or fully ionized form, particularly as a salt or complex.

Still useful herein as crystal growth inhibitor are the organic monophosphonic acids.

Organo monophosphonic acid or one of its salts or complexes is also suitable for use herein as a CGI.

By organo monophosphonic acid it is meant herein an organo monophosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrants.

The organo monophosphonic acid component may be present in its acid form or in the form of one of its salts or complexes with a suitable counter cation. Preferably any salts/complexes are water soluble, with the alkali metal and alkaline earth metal salts/complexes being especially preferred.

A preferred organo monophosphonic acid is 2-phosphonobutane-1,2,4-tricarboxylic acid commercially available from Bayer under the tradename of Bayhibit.

Enzyme

The compositions and processes herein can optionally employ one or more enzymes such as lipases, proteases, cellulase, amylases and peroxidases. A preferred enzyme for use herein is a cellulase enzyme. Indeed, this type of enzyme will further provide a color care benefit to the treated fabric. Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307 discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. Other suitable cellulases are also disclosed in WO

91/17243 to Novo, WO 96/34092, WO 96/34945 and EP-A-0,739,982. In practical terms for current commercial preparations, typical amounts are up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. In the particular cases where activity of the enzyme preparation can be defined otherwise such as with cellulases, corresponding activity units are preferred (e.g. CEVU or cellulase Equivalent Viscosity Units). For instance, the compositions of the present invention can contain cellulase enzymes at a level equivalent to an activity from 0.5 to 1000 CEVU/gram of composition. Cellulase enzyme preparations used for the purpose of formulating the compositions of this invention typically have an activity comprised between 1,000 and 10,000 CEVU/gram in liquid form, around 1,000 CEVU/gram in solid form.

Clay

The compositions of the invention may preferably contain a clay, preferably present at a level of from 0.05% to 40%, more preferably from 0.5% to 30%, most preferably from 2% to 20% by weight of the composition. For clarity, it is noted that the term clay mineral compound, as used herein, excludes sodium aluminosilicate zeolite builder compounds, which however, may be included in the compositions of the invention as optional components.

One preferred clay may be a bentonite clay. Highly preferred are smectite clays, as for example disclosed in the US Patents No.s 3,862,058 3,948,790, 3,954,632 and 4,062,647 and European Patents No.s EP-A-299,575 and EP-A-313,146 all in the name of the Procter and Gamble Company.

The term smectite clays herein includes both the clays in which aluminium oxide is present in a silicate lattice and the clays in which magnesium oxide is present in a silicate lattice. Smectite clays tend to adopt an expandable three layer structure.

Specific examples of suitable smectite clays include those selected from the classes of the montmorillonites, hectorites, volchonskoites, nontronites, saponites and sauconites, particularly those having an alkali or alkaline earth

metal ion within the crystal lattice structure. Sodium or calcium montmorillonite are particularly preferred.

Suitable smectite clays, particularly montmorillonites, are sold by various suppliers including English China Clays, Laviosa, Georgia Kaolin and Colin Stewart Minerals.

Clays for use herein preferably have a particle dimension of from 10nm to 800nm more preferably from 20nm to 500 nm, most preferably from 50nm to 200 nm.

Particles of the clay mineral compound may be included as components of agglomerate particles containing other detergent compounds. Where present as such components, the term "largest particle dimension" of the clay mineral compound refers to the largest dimension of the clay mineral component as such, and not to the agglomerated particle as a whole.

Substitution of small cations, such as protons, sodium ions, potassium ions, magnesium ions and calcium ions, and of certain organic molecules including those having positively charged functional groups can typically take place within the crystal lattice structure of the smectite clays. A clay may be chosen for its ability to preferentially absorb one cation type, such ability being assessed by measurements of relative ion exchange capacity. The smectite clays suitable herein typically have a cation exchange capacity of at least 50 meq/100g. U.S. Patent No. 3,954,632 describes a method for measurement of cation exchange capacity.

The crystal lattice structure of the clay mineral compounds may have, in a preferred execution, a cationic fabric softening agent substituted therein. Such substituted clays have been termed 'hydrophobically activated' clays. The cationic fabric softening agents are typically present at a weight ratio, cationic fabric softening agent to clay, of from 1:200 to 1:10, preferably from 1:100 to 1:20. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

A preferred commercially available "hydrophobically activated" clay is a bentonite clay containing approximately 40% by weight of a dimethyl ditallow quaternary ammonium salt sold under the tradename Claytone EM by English China Clays International.

In a highly preferred embodiment of the invention, the clay is present in an intimate mixture or in a particle with a humectant and a hydrophobic compound, preferably a wax or oil, such as paraffin oil. Preferred humectants are organic compounds, including propylene glycol, ethylene glycol, dimers or trimers of glycol, most preferably glycerol. The particle is preferably an agglomerate. Alternatively, the particle may be such that the wax or oil and optionally the humectant form an encapsulate on the clay or alternatively, the clay be a encapsulate for the wax or oil and the humectant. It may be preferred that the particle comprises an organic salt or silica or silicate.

However, in another embodiment of the invention, the clay is preferably mixed with one or more surfactants and optionally builders and optionally water, in which case the mixture is preferably subsequently dried. Preferably, such a mixture is further processed in a spray-drying method to obtain a spray dried particle comprising the clay.

It may be preferred that the flocculating agent is also comprised in the particle or granule comprising the clay.

It may also be preferred that the intimate mixture comprises a chelating agent.

Flocculating agent

The compositions of the invention may contain a clay flocculating agent, preferably present at a level of from 0.005% to 10%, more preferably from 0.05% to 5%, most preferably from 0.1% to 2% by weight of the composition.

The clay flocculating agent functions such as to bring together the particles of clay compound in the wash solution and hence to aid their deposition onto the surface of the fabrics in the wash. This functional requirement is hence different from that of clay dispersant compounds which are commonly added to laundry

detergent compositions to aid the removal of clay soils from fabrics and enable their dispersion within the wash solution.

Preferred as clay flocculating agents herein are organic polymeric materials having an average weight of from 100,000 to 10,000,000, preferably from 150,000 to 5,000,000, more preferably from 200,000 to 2,000,000.

Suitable organic polymeric materials comprise homopolymers or copolymers containing monomeric units selected from alkylene oxide, particularly ethylene oxide, acrylamide, acrylic acid, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Homopolymers of, on particular, ethylene oxide, but also acrylamide and acrylic acid are preferred.

European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe preferred organic polymeric clay flocculating agents for use herein.

The weight ratio of clay to the flocculating polymer is preferably from 1000:1 to 1:1, more preferably from 500:1 to 1:1, most preferably from 300:1 to 1:1, or even more preferably from 80:1 to 10:1, or in certain applications even from 60:1 to 20:1.

Inorganic clay flocculating agents are also suitable herein, typical examples of which include lime and alum.

The flocculating agent is preferably present in a detergent base granule such as a detergent agglomerate, extrudate or spray-dried particle, comprising generally one or more surfactants and builders.

Effervescent

Effervescent means may also be optionally used in the compositions of the invention.

Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas,



Further examples of acid and carbonate sources and other effervescent systems may be found in : (Pharmaceutical Dosage Forms : Tablets Volume 1 Page 287 to 291).

Carbonate salts

Suitable alkali and/ or earth alkali inorganic carbonate salts herein include carbonate and hydrogen carbonate of potassium, lithium, sodium, and the like amongst which sodium and potassium carbonate are preferred. Suitable bicarbonates to be used herein include any alkali metal salt of bicarbonate like lithium, sodium, potassium and the like, amongst which sodium and potassium bicarbonate are preferred. However, the choice of carbonate or bicarbonate or mixtures thereof may be made depending on the pH desired in the aqueous medium wherein the granules are dissolved. For example where a relative high pH is desired in the aqueous medium (e.g., above pH 9.5) it may be preferred to use carbonate alone or to use a combination of carbonate and bicarbonate wherein the level of carbonate is higher than the level of bicarbonate. The inorganic alkali and/ or earth alkali carbonate salt of the compositions of the invention comprises preferably a potassium or more preferably a sodium salt of carbonate and/ or bicarbonate. Preferably, the carbonate salt comprises sodium carbonate, optionally also a sodium bicarbonate.

The inorganic carbonate salts herein are preferably present at a level of at least 20% by weight of the composition. Preferably they are present at a level of at least 23% or even 25% or even 30% by weight, preferably up to about 60% by weight or more preferably up to 55% or even 50% by weight.

They may be added completely or partially as separate powdered or granular component, as co-granules with other detergent ingredients, for example other salts or surfactants. In solid detergent compositions of the invention, they may also completely or partially be present in detergent granules such as agglomerates or spray dried granules.

In one embodiment of the invention, an effervescence source is present, preferably comprising an organic acid, such as carboxylic acids or aminoacids,

and a carbonate. Then it may be preferred that part or all of the carbonate salt herein is premixed with the organic acid, and thus present in an separate granular component.

Preferred effervescent source are selected from compressed particles of citric acid and carbonate optionally with a binder; and particle of carbonate, bicarbonate and malic or maleic acid in weight ratios of 4:2:4. The dry add form of citric acid and carbonate are preferably used.

The carbonate may have any particle size. In one embodiment, in particular when the carbonate salt is present in a granule and not as separately added compound, the carbonate salt has preferably a volume median particle size from 5 to 375 microns, whereby preferably at least 60%, preferably at least 70% or even at least 80% or even at least 90% by volume, has a particle size of from 1 to 425 microns. More preferably, the carbon dioxide source has a volume median particle size of 10 to 250, whereby preferably at least 60 %, or even at least 70% or even at least 80% or even at least 90% by volume, has a particle size of from 1 to 375 microns; or even preferably a volume median particle size from 10 to 200 microns, whereby preferably at least 60 %, preferably at least 70% or even at least 80% or even at least 90% by volume, has a particle size of from 1 to 250 microns.

In particular when the carbonate salt is added as separate component, so to say 'dry-added' or admixed to the other detergent ingredients, the carbonate may have any particle size, including the above specified particle sizes, but preferably at least an volume average particle size of 200 microns or even 250 microns or even 300 microns.

It may be preferred that the carbon dioxide source of the required particle size is obtained by grinding a larger particle size material, optionally followed by selecting the material with the required particle size by any suitable method.

Whilst percarbonate salts may be present in the compositions of the invention as a bleaching agent, they are not included in the carbonate salts as defined herein

Other preferred optional ingredients include enzyme stabilisers, polymeric soil release agents, materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process (i.e., dye transfer inhibiting agents), polymeric dispersing agents, suds suppressors, optical brighteners or other brightening or whitening agents, anti-static agents, other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations and solid fillers for bar compositions.

Form of the composition

The composition of the invention may take a variety of physical form including liquid, gel, foam in either aqueous or non-aqueous form, granular and tablet forms.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

Granular detergents can be prepared, for example, by spray-drying (final product density 520 g/l) or agglomerating (final product density above 600 g/l) the Base Granule. The remaining dry ingredients can then be admixed in granular or powder form with the Base Granule, for example in a rotary mixing drum, and the liquid ingredients (e.g., nonionic surfactant and perfume) can be sprayed on.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between 6.5 and 11, preferably between 7.5 and 10.5. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well-known to those skilled in the art.

When in a liquid form, the composition may also be dispensed by a dispensing means such as a spray dispenser, or aerosol dispenser.

Spray Dispenser

The present invention also relates to such compositions incorporated into a spray dispenser to create an article of manufacture that can facilitate treatment of fabric articles and/or surfaces with said compositions containing the amine reaction product and other ingredients (examples are cyclodextrins, polysaccharides, polymers, surfactant, perfume, softener) at a level that is effective, yet is not discernible when dried on the surfaces. The spray dispenser comprises manually activated and non-manual powered (operated) spray means and a container containing the treating composition. Typical disclosure of such spray dispenser can be found in WO 96/04940 page 19 line 21 to page 22 line 27. The articles of manufacture preferably are in association with instructions for use to ensure that the consumer applies sufficient ingredient of the composition to provide the desired benefit. Typical compositions to be dispensed from a sprayer contain a level of amine reaction product of from about 0.01% to about 5%, preferably from about 0.05% to about 2%, more preferably from about 0.1% to about 1%, by weight of the usage composition.

Method of use

The composition of the invention are suitable for use in any step of the domestic treatment, that is a pre-treatment composition, as a wash additive, as a composition suitable for use in the laundry and cleaning process. Obviously, multiple application can be made such as treating the fabric with a pre-treatment composition of the invention and thereafter with the composition suitable for use in the laundry process.

Also provided herein is a method for providing a delayed release of an active ketone or aldehyde which comprises the step of contacting the surface to be treated with a compound or composition of the invention, and thereafter contacting the treated surface with a material, preferably an aqueous medium like moisture or any other means susceptible of releasing the perfume from the amine reaction product.

By "surface", it is meant any surface onto which the compound can deposit. Typical examples of such material are fabrics, hard surfaces such as dishware, floors, bathrooms, toilet, kitchen and other surfaces in need of a delayed release of a perfume ketone and/or aldehyde such as that with litter like animal litter. Preferably, the surface is selected from a fabric, a tile, a ceramic; more preferably is a fabric.

By "delayed release" is meant release of the active component (e.g perfume) over a longer period of time than by the use of the active (e.g., perfume) itself.

Abbreviations used in the following laundry and cleaning composition Examples

In the laundry and cleaning compositions, the abbreviated component identifications have the following meanings:

In the detergent compositions, the abbreviated component identifications have the following meanings:

| | |
|----------------------------------|---|
| LAS | : Sodium linear C ₁₁₋₁₃ alkyl benzene sulfonate |
| TAS | : Sodium tallow alkyl sulfate |
| C _{xy} AS | : Sodium C _{1x} - C _{1y} alkyl sulfate |
| C ₄₆ SAS | : Sodium C ₁₄ - C ₁₆ secondary (2,3) alkyl sulfate |
| C _{xy} E _z S | : Sodium C _{1x} -C _{1y} alkyl sulfate condensed with z moles of ethylene oxide |
| C _{xy} E _z | : C _{1x} -C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide |
| QAS | : R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ - C ₁₄ |
| QAS 1 | : R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₈ - C ₁₁ |
| APA | : C ₈ - C ₁₀ amido propyl dimethyl amine |
| Soap | : Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids |
| STS | : Sodium toluene sulphonate |
| CFAA | : C ₁₂ -C ₁₄ (coco) alkyl N-methyl glucamide |
| TFAA | : C ₁₆ -C ₁₈ alkyl N-methyl glucamide |
| TPKFA | : C ₁₂ -C ₁₄ topped whole cut fatty acids |
| STPP | : Anhydrous sodium tripolyphosphate |

| | |
|-----------------|---|
| TSPP | : Tetrasodium pyrophosphate |
| Zeolite A | : Hydrated sodium aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis) |
| NaSKS-6 | : Crystalline layered silicate of formula $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ |
| Citric acid | : Anhydrous citric acid |
| Borate | : Sodium borate |
| Carbonate | : Anhydrous sodium carbonate with a particle size between 200 μm and 900 μm |
| Bicarbonate | : Anhydrous sodium bicarbonate with a particle size distribution between 400 μm and 1200 μm |
| Silicate | : Amorphous sodium silicate ($\text{SiO}_2\text{:Na}_2\text{O} = 2.0\text{:}1$) |
| Sulfate | : Anhydrous sodium sulfate |
| Mg sulfate | : Anhydrous magnesium sulfate |
| Citrate | : Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 μm and 850 μm |
| MA/AA | : Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000 |
| MA/AA (1) | : Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000 |
| AA | : Sodium polyacrylate polymer of average molecular weight 4,500 |
| CMC | : Sodium carboxymethyl cellulose |
| Cellulose ether | : Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals |
| Protease | : Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase |
| Protease I | : Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc. |
| Alcalase | : Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S |

| | |
|---------------------------|--|
| Cellulase | : Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme |
| Amylase | : Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T |
| Lipase | : Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase |
| Lipase (1) | : Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra |
| Endolase | : Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S |
| PB4 | : Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$ |
| PB1 | : Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$ |
| Percarbonate | : Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ |
| NOBS | : Nonanoyloxybenzene sulfonate in the form of the sodium salt |
| NAC-OBS | : (6-nonamidocaproyl) oxybenzene sulfonate |
| TAED | : Tetraacetythylenediamine |
| DTPA | : Diethylene triamine pentaacetic acid |
| DTPMP | : Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060 |
| EDDS | : Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt. |
| Photoactivated bleach (1) | : Sulfonated zinc phthlocyanine encapsulated in dextrin soluble polymer |
| Photoactivated bleach (2) | : Sulfonated alumino phthlocyanine encapsulated in dextrin soluble polymer |
| Brightener 1 | : Disodium 4,4'-bis(2-sulphostyryl)biphenyl |

| | |
|-------------------|---|
| Brightener 2 | : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate |
| HEDP | : 1,1-hydroxyethane diphosphonic acid |
| PEGx | : Polyethylene glycol, with a molecular weight of x (typically 4,000) |
| PEO | : Polyethylene oxide, with an average molecular weight of 50,000 |
| TEPAE | : Tetraethylenepentaamine ethoxylate |
| PVI | : Polyvinyl imidosole, with an average molecular weight of 20,000 |
| PVP | : Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000 |
| PVNO | : Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000 |
| PVPVI | : Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000 |
| QEA | : bis((C ₂ H ₅ O)(C ₂ H ₄ O) _n)(CH ₃) -N ⁺ -C ₆ H ₁₂ -N ⁺ -(CH ₃) bis((C ₂ H ₅ O)-(C ₂ H ₄ O)) _n , wherein n = from 20 to 30 |
| SRP 1 | : Anionically end capped poly esters |
| SRP 2 | : Diethoxylated poly (1, 2 propylene terephtalate) short block polymer |
| PEI | : Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen |
| Silicone antifoam | : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1 |
| Opacifier | : Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621 |
| Wax | : Paraffin wax |
| PA30 | : Polyacrylic acid of average molecular weight of between about 4,500 - 8,000. |
| 480N | : Random copolymer of 7:3 acrylate/methacrylate, average molecular weight about 3,500. |
| Polygel/carbopol | : High molecular weight crosslinked polyacrylates. |

| | |
|------------------------|--|
| Metasilicate | : Sodium metasilicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio = 1.0). |
| Nonionic | : C ₁₃ -C ₁₅ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5. |
| Neodol 45-13 | : C ₁₄ -C ₁₅ linear primary alcohol ethoxylate, sold by Shell Chemical CO. |
| MnTACN | : Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane. |
| PAAC | : Pentaamine acetate cobalt(III) salt. |
| Paraffin | : Paraffin oil sold under the tradename Winog 70 by Wintershall. |
| NaBz | : Sodium benzoate. |
| BzP | : Benzoyl Peroxide. |
| SCS | : Sodium cumene sulphonate. |
| BTA | : Benzotriazole. |
| pH | : Measured as a 1% solution in distilled water at 20°C. |
| ARP1 | : Amine reaction product of ethyl 4-aminobenzoate with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde as made from Synthesis example I |
| ARP2 | : Amine reaction product of Lupasol P with α -Damascone as made from Synthesis example III |
| ARP3 | : Amine reaction product of D-glucamine with Citronellal as made from Synthesis example II |
| ARP4 | : Amine reaction product of tyrosine ethylate with α -Damascone as made from Synthesis example IV method b |
| ARP5 | : Amine reaction product of tyrosine ethylate with Hexyl Cinnamic Aldehyde made according to Synthesis example IV method b |
| ARP6 | : Amine reaction product of Lupasol HF with δ -Damascone as made from Synthesis example III |
| Clay I | : Bentonite clay |
| Clay II | : Smectite clay |
| Flocculating agent I: | polyethylene oxide of average molecular weight of between 200,000 and 400,000 |
| Flocculating agent II: | polyethylene oxide of average molecular weight of between 400,000 and 1,000,000 |

| | |
|-------------------------|---|
| Flocculating agent III: | polymer of acrylamide and/ or acrylic acid of average molecular weight of 200,000 and 400,000 |
| DOBS: | Decanoyl oxybenzene sulfonate in the form of the sodium salt |
| SRP 3 | : Polysaccharide soil release polymer |
| SRP 4 | : Nonionically end capped poly esters |

The following are synthesis examples of compounds as defined in the present invention:

I-Synthesis of ethyl 4-aminobenzoate with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde

To an ice cooled stirred solution of 10 g of 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde (0.07 mol) in 35 mL EtOH and molecular sieves (4Å, 20 g) 1eq of the amine was added via an addition funnel. The reaction mixture was stirred under nitrogen atmosphere and protected from light. After 6 days the mixture was filtrated and the solvent was removed. The yield of imine formation is about 90%.

Similar results were obtained where the 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde was replaced by bourgeonal, or trans-2-nonenal.

II-Synthesis of D-glucamine with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde

To an ice cooled solution of 1 mmol D-glucamine in about 30 mL EtOH and molecular sieves (4Å, 5 g) 1eq of the 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde was added. The reaction was stirred under nitrogen atmosphere and protected from light. After 3 to 4 days, the molecular sieves and the solvent were removed by filtration and evaporation respectively. The solid imine was obtained in 85 to 90% yield.

Similar results were obtained where the 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde was replaced by citronellal, trans-2-nonenal, or decanal.

III-Synthesis of Lupasol with Damascone

The β -amino ketone from Lupasol G100 (commercially available by BASF content 50 % water, 50 % Lupasol G100 (Mw. 5000)) and α -Damascone was prepared using any one of these three different procedures described as follows:

1. Commercially available Lupasol G100 was dried using the following procedure: 20 g of the Lupasol solution was dried at the rotating evaporator during several hours. The obtained residue, still containing about 4.5 g of H_2O , was azeotropically distilled at the rotating evaporator using toluene. The residue was then placed in the desiccator dried at 60 °C (using P_2O_5 as water absorbing material). On basis of the obtained weight we concluded that the oil contained less than 10 % H_2O . On basis of the NMR-spectra we concluded that this is probably less than 5 %. This dried sample was then used in the preparation of β -amino ketones.

1.38 g of the dried Lupasol G100 obtained above was dissolved in 7 ml. ethanol. The solution was stirred gently with a magnetic stirrer during a few minutes before 2 g Na_2SO_4 (anhydrous) was added. After stirring again for a few minutes 2.21 g α -Damascone was added over a period of 1 minute. After two days reaction, the mixture was filtrated over a Celite filter (vide supra), and the residue washed thoroughly with ethanol. About 180 ml. of a light foaming filtrate was obtained. This was concentrated until dryness using a rotating evaporator and dried over P_2O_5 in an desiccator at room temperature. About 3.5 of a colorless oil was obtained.

2. 4.3 g Lupasol G100 solution was (without drying) dissolved in 10 ml. ethanol. The solution was stirred with a magnetic stirrer during a few minutes before 3.47 g α -Damascone was added over a 1.5 minutes period. After two days reaction at room temperature the reaction mixture was filtrated over Celite (vide supra) and the residue washed thoroughly with ethanol. The filtrate (200 ml., light foaming) was concentrated at the evaporator and dried in an desiccator (P_2O_5 as drying agent) at room temperature. About 5.9 g of a colorless oil was obtained.
3. To 3.0 g of Lupasol G100 solution (used as such) was added 2.41 g α -Damascone. The mixture was stirred without using solvent. After stirring for 4 days the obtained oil was dissolved in 100 ml. THF, dried with $MgSO_4$,

filtrated and the filtrate concentrated at the rotating evaporator. After drying in the desiccator (P_2O_5) at room temperature, about 4.1 g of a colorless oil was obtained. This oil still contained about 13 % (w/w) of THF, even after a prolonged drying (3 days).

The product obtained from the three procedures had identical NMR-spectra.

Still another possible route of synthesis is by using Lupasol P or Lupasol HF. The β -amino ketone from Lupasol P and α -Damascone was prepared using the procedure described as follows:

1.8g Lupasol P solution (50 % H_2O , 50 % Lupasol Mw. 750000, as obtained from BASF) was dissolved in 7 ml ethanol, the solution was stirred for a few minutes with a magnetic stirrer before 1.44 g α -Damascone was added. After three days the reaction mixture was filtrated over a celite filter (vide supra) and the residue washed thoroughly with ethanol. After concentrating of the filtrate and drying of the obtained oil in the desiccator (P_2O_5) at room temperature, about 3 g of the reaction product between Lupasol and α -Damascone was obtained.

IV- Synthesis of L-Tyrosine ethylate and Damascone

The amine reaction product between L-Tyrosine ethylate and Damascone was prepared using the procedure described as follows:

a)- L-Tyrosine ethyl ester (2.09 g) and Damascone (1.92 g) in CH_2Cl_2 (10 ml) and molecular sieves (4Å, 5 g) were mixed together with stirring. The reaction between L-Tyrosine ethyl ester and Damascone in CH_2Cl_2 and molecular sieves is followed with mass spectroscopy. After 24 hours, formation of the β -aminoketone has been found. The solvent is evaporated and a viscous liquid is obtained. The NMR shows small amounts of unreacted Damascone (8%).

b)- L-Tyrosine ethyl ester (2.09 g) and Damascone (1.92 g) in CH_2Cl_2 (10 ml) were mixed together with stirring. The reaction between L-Tyrosine ethyl ester and Damascone in CH_2Cl_2 is followed with mass spectroscopy. After 24h formation of β -aminoketone is observed. The solvent is evaporated and a

viscous oil is obtained. The NMR shows small amounts of unreacted Damascone (6%).

Similarly, the synthesis between Hexyl Cinnamic Aldehyde and L-Tyrosine ethyl ester is performed according to either of the methods above described.

In the following formulation examples all levels are quoted as % by weight of the composition unless otherwise stated, and incorporation of the amine reaction product so called herein after "ARP" in the fully formulated composition is carried out by dry addition (d), spray on (s), encapsulation in starch (es) as described in GB-1,464,616 or cyclodextrin (ec) or as is in the composition as defined herein before. The term in bracket for the ARP in the formulation examples refers to the means of incorporation. When none is provided, the incorporation is made as it is.

Example 1

The following high density granular laundry detergent compositions A to G were prepared in accord with the invention:

| | A | B | C | D | E | F | G |
|-------------|------|------|------|------|------|------|------|
| LAS | 8.0 | 8.0 | 8.0 | 2.0 | 6.0 | 6.0 | 5.0 |
| TAS | - | 0.5 | - | 0.5 | 1.0 | 0.1 | 1.5 |
| C46(S)AS | 2.0 | 2.5 | - | - | - | - | - |
| C25AS | - | - | - | 7.0 | 4.5 | 5.5 | 2.5 |
| C68AS | 2.0 | 5.0 | 7.0 | - | - | - | 0.2 |
| C25E5 | - | - | 3.4 | 10.0 | 4.6 | 4.6 | 2.6 |
| C25E7 | 3.4 | 3.4 | 1.0 | - | - | - | - |
| C25E3S | - | - | - | 2.0 | 5.0 | 4.5 | 0.5 |
| QAS | - | 0.8 | - | - | - | - | - |
| QAS (I) | - | - | - | 0.8 | 0.5 | 1.0 | 1.5 |
| Zeolite A | 18.1 | 18.0 | 14.1 | 18.1 | 20.0 | 18.1 | 16.2 |
| Citric acid | - | - | - | 2.5 | - | 2.5 | 1.5 |
| Carbonate | 13.0 | 13.0 | 27.0 | 10.0 | 10.0 | 13.0 | 20.6 |
| SKS-6 | - | - | - | 10.0 | - | 10.0 | 4.3 |
| Silicate | 1.4 | 1.4 | 3.0 | 0.3 | 0.5 | 0.3 | - |
| Citrate | - | 1.0 | - | 3.0 | - | - | 1.4 |

| | A | B | C | D | E | F | G |
|------------------------------------|-----------|-----------|-----------|----------|-----------|-----------|---------|
| Sulfate | 26.1 | 26.1 | 26.1 | 6.0 | - | - | - |
| Mg sulfate | 0.3 | - | - | 0.2 | - | 0.2 | 0.03 |
| MA/AA | 0.3 | 0.3 | 0.3 | 4.0 | 1.0 | 1.0 | 0.6 |
| CMC | 0.2 | 0.2 | 0.2 | 0.2 | 0.4 | 0.4 | 0.3 |
| PB4 | 9.0 | 9.0 | 5.0 | - | - | - | - |
| Percarbonat e | - | - | - | - | 18.0 | 18.0 | 9.0 |
| TAED | 1.5 | 0.4 | 1.5 | - | 3.9 | 4.2 | 3.2 |
| NAC-OBS | - | 2.0 | 1.0 | - | - | - | - |
| DTPMP | 0.25 | 0.25 | 0.25 | 0.25 | - | - | - |
| SRP 2 | - | - | - | 0.2 | - | 0.2 | - |
| EDDS | - | 0.25 | 0.4 | - | 0.5 | 0.5 | 0.1 |
| TFAA | - | - | - | - | - | - | 1.1 |
| CFAA | - | 1.0 | - | 2.0 | - | - | - |
| HEDP | 0.3 | 0.3 | 0.3 | 0.3 | 0.4 | 0.4 | 0.3 |
| QEA | - | - | - | 0.2 | - | 0.5 | - |
| Protease I | - | - | 0.26 | 1.0 | - | - | 0.3 |
| Protease | 0.26 | 0.26 | - | - | 1.5 | 1.0 | - |
| Cellulase | 0.3 | - | - | 0.3 | 0.3 | 0.3 | 0.3 |
| Amylase | 0.1 | 0.1 | 0.1 | 0.4 | 0.5 | 0.5 | 0.1 |
| Lipase (1) | 0.3 | - | - | 0.5 | 0.5 | 0.5 | 0.1 |
| Photoactivat ed bleach (ppm) | 15 ppm | 15 ppm | 15 ppm | - | 20 ppm | 20 ppm | 20 ppm |
| PVNO/PVPV I | - | - | - | 0.1 | - | - | - |
| Brightener 1 | 0.09 | 0.09 | 0.09 | - | 0.09 | 0.09 | 0.01 |
| Brightener 2 | - | - | - | - | - | - | 0.09 |
| Perfume spray on | 0.3 | 0.3 | 0.3 | 0.4 | 0.4 | 0.4 | 0.4 |
| ARP 1 | 0.3(d) | 0.1(es) | - | - | 0.1(d) | 0.5(ec) | - |
| ARP 2 | - | - | 0.04(s) | 0.04(ec) | 0.02(s) | - | - |
| ARP 6 | - | - | - | - | - | - | 0.4(es) |

| | A | B | C | D | E | F | G |
|----------------------|-----|-----|-----|-----|-----|-----|------|
| Silicone antifoam | 0.5 | 0.5 | 0.5 | - | 0.3 | 0.3 | 0.3 |
| Clay II | - | - | - | - | - | - | 12.0 |
| Flocculating agent I | - | - | - | - | - | - | 0.3 |
| Glycerol | - | - | - | - | - | - | 0.6 |
| Wax | - | - | - | - | - | - | 0.4 |
| Misc/minors to 100% | | | | | | | |
| Density in g/litre | 850 | 850 | 850 | 850 | 850 | 850 | 850 |

Example 2

The following granular laundry detergent compositions of particular utility under European machine wash conditions were prepared in accord with the invention:

| | A | B | C | D | E | F |
|--------------------------------|------|------|------|------|------|------|
| LAS | 5.5 | 7.5 | 5.0 | 5.0 | 6.0 | 7.0 |
| TAS | 1.25 | 1.86 | - | 0.8 | 0.4 | 0.3 |
| C24AS/C25AS | - | 2.24 | 5.0 | 5.0 | 5.0 | 2.2 |
| C25E3S | - | 0.76 | 1.0 | 1.5 | 3.0 | 1.0 |
| C45E7 | 3.25 | - | - | - | - | 3.0 |
| TFAA | - | - | 2.0 | - | - | - |
| C25E5 | - | 5.5 | - | - | - | - |
| QAS | 0.8 | - | - | - | - | - |
| QAS II | - | 0.7 | 1.0 | 0.5 | 1.0 | 0.7 |
| STPP | 19.7 | - | - | - | - | - |
| Zeolite A | - | 19.5 | 25.0 | 19.5 | 20.0 | 17.0 |
| NaSKS-6/citric acid (79:21) | - | 10.6 | - | 10.6 | - | - |
| NaSKS-6 | - | - | 9.0 | - | 10.0 | 10.0 |
| Carbonate | 6.1 | 21.4 | 9.0 | 10.0 | 10.0 | 18.0 |
| Bicarbonate | - | 2.0 | 7.0 | 5.0 | - | 2.0 |
| Silicate | 6.8 | - | - | 0.3 | 0.5 | - |
| Citrate | - | - | 4.0 | 4.0 | - | - |
| Sulfate | 39.8 | - | - | 5.0 | - | 12.0 |
| Mg sulfate | - | - | 0.1 | 0.2 | 0.2 | - |
| MA/AA | 0.5 | 1.6 | 3.0 | 4.0 | 1.0 | 1.0 |
| CMC | 0.2 | 0.4 | 1.0 | 1.0 | 0.4 | 0.4 |
| PB4 | 5.0 | 12.7 | - | - | - | - |
| Percarbonate | - | - | - | - | 18.0 | 15.0 |
| TAED | 0.5 | 3.1 | - | - | 5.0 | - |
| NAC-OBS | 1.0 | 3.5 | - | - | - | 2.5 |
| DTPMP | 0.25 | 0.2 | 0.3 | 0.4 | - | 0.2 |
| HEDP | - | 0.3 | - | 0.3 | 0.3 | 0.3 |
| QEA | - | - | 1.0 | 1.0 | 1.0 | - |
| Protease I | - | - | - | 0.5 | 1.2 | - |

| | A | B | C | D | E | F |
|------------------------------------|-------------------|-----------|---------|----------|-----------|-----------|
| Protease | 0.26 | 0.85 | 0.9 | 1.0 | - | 0.7 |
| Lipase (1) | 0.15 | 0.15 | 0.3 | 0.3 | 0.3 | 0.2 |
| Cellulase | 0.28 | 0.28 | 0.2 | 0.2 | 0.3 | 0.3 |
| Amylase | 0.1 | 0.1 | 0.4 | 0.4 | 0.6 | 0.2 |
| PVNO/PVPVI | - | - | 0.2 | 0.2 | - | - |
| PVP | 0.9 | 1.3 | - | - | - | 0.9 |
| SRP 1 | - | - | 0.2 | 0.2 | 0.2 | - |
| Photoactivated bleach (1) (ppm) | 15 ppm | 27 ppm | - | - | 20 ppm | 20 ppm |
| Photoactivated bleach (2) (ppm) | 15 ppm | - | - | - | - | - |
| Brightener 1 | 0.08 | 0.19 | - | - | 0.09 | 0.15 |
| Brightener 2 | - | 0.04 | - | - | - | - |
| Perfume | 0.3 | 0.3 | 0.4 | 0.3 | 0.4 | 0.3 |
| ARP1 | 0.1(d) 0.1(es) | 1.0(d) | - | - | - | 0.1(es) |
| ARP2 | - | - | 0.04(s) | 0.02(ec) | 0.04(d) | 0.02(es) |
| Silicone antifoam | 0.5 | 2.4 | 0.3 | 0.5 | 0.3 | 2.0 |
| Minors/misc to 100% | | | | | | |
| Density in g/litre | 750 | 750 | 750 | 750 | 750 | 750 |

Example 3

The following detergent formulations of particular utility under European machine wash conditions were prepared in accord with the invention.

| | A | B | C | D |
|----------------------|----------|----------|----------|----------|
| Blown powder | | | | |
| LAS | 6.0 | 5.0 | 11.0 | 6.0 |
| TAS | 2.0 | - | - | 2.0 |
| Zeolite A | 24.0 | - | - | 20.0 |
| STPP | - | 27.0 | 24.0 | - |
| Sulfate | 4.0 | 6.0 | 13.0 | - |
| MA/AA | 1.0 | 4.0 | 6.0 | 2.0 |
| Silicate | 1.0 | 7.0 | 3.0 | 3.0 |
| CMC | 1.0 | 1.0 | 0.5 | 0.6 |
| Brightener 1 | 0.2 | 0.2 | 0.2 | 0.2 |
| Silicone antifoam | 1.0 | 1.0 | 1.0 | 0.3 |
| DTPMP | 0.4 | 0.4 | 0.2 | 0.4 |
| Spray on | | | | |
| Brightener | 0.02 | - | - | 0.02 |
| C45E7 | - | - | - | 5.0 |
| C45E2 | 2.5 | 2.5 | 2.0 | - |
| C45E3 | 2.6 | 2.5 | 2.0 | - |
| Perfume | 0.5 | 0.3 | 0.5 | 0.2 |
| Silicone antifoam | 0.3 | 0.3 | 0.3 | - |
| Dry additives | | | | |
| QEA | - | - | - | 1.0 |
| EDDS | 0.3 | - | - | - |
| Sulfate | 2.0 | 3.0 | 5.0 | 10.0 |
| Carbonate | 6.0 | 13.0 | 15.0 | 14.0 |
| Citric acid | 2.5 | - | - | 2.0 |
| QAS II | 0.5 | - | - | 0.5 |
| SKS-6 | 10.0 | - | - | - |
| Percarbonate | 18.5 | - | - | - |
| PB4 | - | 18.0 | 10.0 | 21.5 |
| TAED | 2.0 | 2.0 | - | 2.0 |

| | A | B | C | D |
|---------------------------|----------|----------|----------|----------|
| NAC-OBS | 3.0 | 2.0 | 4.0 | - |
| Protease | 1.0 | 1.0 | 1.0 | 1.0 |
| Lipase | - | 0.4 | - | 0.2 |
| Lipase (1) | 0.4 | - | 0.4 | - |
| Amylase | 0.2 | 0.2 | 0.2 | 0.4 |
| Brightener 1 | 0.05 | - | - | 0.05 |
| ARP3 | 0.3 | 0.1(es) | 1.0 | 0.05(ec) |
| Misc/minor to 100% | | | | |

Example 4

The following granular detergent formulations were prepared in accord with the invention.

| | A | B | C | D | E | F |
|----------------------|--------|---------|------|------|------|------|
| Blown powder | | | | | | |
| LAS | 23.0 | 8.0 | 7.0 | 9.0 | 7.0 | 7.0 |
| TAS | - | - | - | - | 1.0 | - |
| C45AS | 6.0 | 6.0 | 5.0 | 8.0 | - | - |
| C45AES | - | 1.0 | 1.0 | 1.0 | - | - |
| C45E35 | - | - | - | - | 2.0 | 4.0 |
| Zeolite A | 10.0 | 18.0 | 14.0 | 12.0 | 10.0 | 10.0 |
| MA/AA | - | 0.5 | - | - | - | 2.0 |
| MA/AA (1) | 7.0 | - | - | - | - | - |
| AA | - | 3.0 | 3.0 | 2.0 | 3.0 | 3.0 |
| Sulfate | 5.0 | 6.3 | 14.3 | 11.0 | 15.0 | 19.3 |
| Silicate | 10.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Carbonate | 15.0 | 20.0 | 10.0 | 20.7 | 8.0 | 6.0 |
| PEG 4000 | 0.4 | 1.5 | 1.5 | 1.0 | 1.0 | 1.0 |
| DTPA | - | 0.9 | 0.5 | - | - | 0.5 |
| Brightener 2 | 0.3 | 0.2 | 0.3 | - | 0.1 | 0.3 |
| Spray on | | | | | | |
| C45E7 | - | 2.0 | - | - | 2.0 | 2.0 |
| C25E9 | 3.0 | - | - | - | - | - |
| C23E9 | - | - | 1.5 | 2.0 | - | 2.0 |
| Perfume | 0.3 | 0.3 | 0.3 | 2.0 | 0.3 | 0.3 |
| ARP5 | 0.1(s) | 0.05(s) | - | - | - | - |
| Agglomerates | | | | | | |
| C45AS | - | 5.0 | 5.0 | 2.0 | - | 5.0 |
| LAS | - | 2.0 | 2.0 | - | - | 2.0 |
| Zeolite A | - | 7.5 | 7.5 | 8.0 | - | 7.5 |
| Carbonate | - | 4.0 | 4.0 | 5.0 | - | 4.0 |
| PEG 4000 | - | 0.5 | 0.5 | - | - | 0.5 |
| Misc (water etc) | - | 2.0 | 2.0 | 2.0 | - | 2.0 |
| Dry additives | | | | | | |

| | A | B | C | D | E | F |
|----------------------|-----|-----|--------|-----|---------|---------|
| QAS (I) | - | - | - | - | 1.0 | - |
| Citric acid | - | - | - | - | 2.0 | - |
| PB4 | - | - | - | - | 12.0 | 1.0 |
| PB1 | 4.0 | 1.0 | 3.0 | 2.0 | - | - |
| Percarbonate | - | - | - | - | 2.0 | 10.0 |
| Carbonate | - | 5.3 | 1.8 | - | 4.0 | 4.0 |
| NOBS | 4.0 | - | 6.0 | - | - | 0.6 |
| Methyl cellulose | 0.2 | - | - | - | - | - |
| SKS-6 | 8.0 | - | - | - | - | - |
| STS | - | - | 2.0 | - | 1.0 | - |
| Cumene sulfonic acid | - | 1.0 | - | - | - | 2.0 |
| Lipase | 0.2 | - | 0.2 | - | 0.2 | 0.4 |
| Cellulase | 0.2 | 0.2 | 0.2 | 0.3 | 0.2 | 0.2 |
| Amylase | 0.2 | - | 0.1 | - | 0.2 | - |
| Protease | 0.5 | 0.5 | 0.5 | 0.3 | 0.5 | 0.5 |
| PVPVI | - | - | - | - | 0.5 | 0.1 |
| PVP | - | - | - | - | 0.5 | - |
| PVNO | - | - | 0.5 | 0.3 | - | - |
| QEA | - | - | - | - | 1.0 | - |
| SRP1 | 0.2 | 0.5 | 0.3 | - | 0.2 | - |
| ARP6 | - | - | 0.1(d) | 0.1 | 0.4(es) | 0.4(es) |
| Silicone antifoam | 0.2 | 0.4 | 0.2 | 0.4 | 0.1 | - |
| Mg sulfate | - | - | 0.2 | - | 0.2 | - |
| Misc/minors to 100% | | | | | | |

| | G | H | I | J |
|--------------|------|------|------|------|
| Blown powder | | | | |
| Clay I or II | 7.0 | 10.0 | 6.0 | 2.0 |
| LAS | 16.0 | 5.0 | 11.0 | 6.0 |
| TAS | - | 5.0 | - | 2.0 |
| Zeolite A | - | 20.0 | - | 10.0 |
| STPP | 24.0 | - | 14.0 | - |
| Sulfate | - | 2.0 | - | - |

| | | | | |
|----------------------------|------|---------|----------|------|
| MA/AA | - | 2.0 | 1.0 | 1.0 |
| Silicate | 4.0 | 7.0 | 3.0 | - |
| CMC | 1.0 | - | 0.5 | 0.6 |
| Brightener 1 | 0.2 | 0.2 | 0.2 | 0.2 |
| Carbonate | 10.0 | 10.0 | 20.0 | - |
| DTPMP | 0.4 | 0.4 | 0.2 | - |
| Spray on | | | | |
| Brightener 1 | 0.02 | - | - | 0.02 |
| C45E7 or E9 | - | - | 2.0 | 1.0 |
| C45E3 or E4 | - | - | 2.0 | 4.0 |
| Perfume | 0.5 | - | 0.5 | 0.2 |
| Silicone antifoam | 0.3 | - | - | - |
| Dry additives | | | | |
| Flocculating agent I or II | 0.3 | 1.0 | 1.0 | 0.5 |
| QEA | - | - | - | 1.0 |
| HEDP/ EDDS | 0.3 | - | - | - |
| Sulfate | 2.0 | - | - | - |
| Carbonate | 20.0 | 13.0 | 15.0 | 24.0 |
| Citric acid | 2.5 | - | - | 2.0 |
| QAS | - | - | 0.5 | 0.5 |
| NaSKS-6 | 3.5 | - | - | 5.0 |
| Percarbonate | - | - | - | 9.0 |
| PB4 | - | - | 5.0 | |
| NOBS | - | - | - | 1.3 |
| TAED | - | - | 2.0 | 1.5 |
| Protease | 1.0 | 1.0 | 1.0 | 1.0 |
| Lipase | - | 0.4 | - | 0.2 |
| Amylase | 0.2 | 0.2 | 0.2 | 0.4 |
| Brightener 2 | 0.05 | - | - | 0.05 |
| Perfume | 1.0 | 0.2 | 0.5 | 0.3 |
| Speckle | 1.2 | 0.5 | 2.0 | - |
| ARP 6 | 0.08 | 1.5 (d) | 3.0 (es) | - |
| ARP 1 | - | - | - | 0.1 |
| Misc/minor to 100% | | | | |

Example 5

The following nil bleach-containing detergent formulations of particular use in the washing of coloured clothing, according to the present invention were prepared:

| | A | B | C |
|----------------------|----------|----------|----------|
| Blown Powder | | | |
| Zeolite A | 15.0 | 15.0 | - |
| Sulfate | 0.0 | 5.0 | - |
| LAS | 3.0 | 3.0 | - |
| DTPMP | 0.4 | 0.5 | - |
| CMC | 0.4 | 0.4 | - |
| MA/AA | 4.0 | 4.0 | - |
| Agglomerates | | | |
| C45AS | - | - | 11.0 |
| LAS | 6.0 | 5.0 | - |
| TAS | 3.0 | 2.0 | - |
| Silicate | 4.0 | 4.0 | - |
| Zeolite A | 10.0 | 15.0 | 13.0 |
| CMC | - | - | 0.5 |
| MA/AA | - | - | 2.0 |
| Carbonate | 9.0 | 7.0 | 7.0 |
| Spray On | | | |
| Perfume | 0.3 | 0.3 | 0.5 |
| C45E7 | 4.0 | 4.0 | 4.0 |
| C25E3 | 2.0 | 2.0 | 2.0 |
| ARP2 | 0.04(s) | - | - |
| Dry additives | | | |
| MA/AA | - | - | 3.0 |
| NaSKS-6 | - | - | 12.0 |
| Citrate | 10.0 | - | 8.0 |
| Bicarbonate | 7.0 | 3.0 | 5.0 |
| Carbonate | 8.0 | 5.0 | 7.0 |
| PVPVI/PVNO | 0.5 | 0.5 | 0.5 |
| Alcalase | 0.5 | 0.3 | 0.9 |
| Lipase | 0.4 | 0.4 | 0.4 |

| | A | B | C |
|----------------------------|----------|----------|----------|
| Amylase | 0.6 | 0.6 | 0.6 |
| Cellulase | 0.6 | 0.6 | 0.6 |
| ARP1 | - | 0.3 | 0.1(es) |
| Silicone antifoam | 5.0 | 5.0 | 5.0 |
| Dry additives | | | |
| Sulfate | 0.0 | 9.0 | 0.0 |
| Misc/minors to 100% | 100.0 | 100.0 | 100.0 |
| Density (g/litre) | 700 | 700 | 700 |

Example 6

The following granular detergent formulations were prepared in accord with the invention.

| | A | B | C | D |
|----------------------|---------|------|------|------|
| Base granule | | | | |
| Zeolite A | 30.0 | 22.0 | 24.0 | 10.0 |
| Sulfate | 10.0 | 5.0 | 10.0 | 7.0 |
| MA/AA | 3.0 | - | - | - |
| AA | - | 1.6 | 2.0 | - |
| MA/AA (1) | - | 12.0 | - | 6.0 |
| LAS | 14.0 | 10.0 | 9.0 | 20.0 |
| C45AS | 8.0 | 7.0 | 9.0 | 7.0 |
| C45AES | - | 1.0 | 1.0 | - |
| Silicate | - | 1.0 | 0.5 | 10.0 |
| Soap | - | 2.0 | - | - |
| Brightener 1 | 0.2 | 0.2 | 0.2 | 0.2 |
| Carbonate | 6.0 | 9.0 | 10.0 | 10.0 |
| PEG 4000 | - | 1.0 | 1.5 | - |
| DTPA | - | 0.4 | - | - |
| Spray on | | | | |
| C25E9 | - | - | - | 5.0 |
| C45E7 | 1.0 | 1.0 | - | - |
| C23E9 | - | 1.0 | 2.5 | - |
| Perfume | 0.2 | 0.3 | 0.3 | - |
| ARP2 | 0.04(s) | - | - | - |
| Dry additives | | | | |
| Carbonate | 5.0 | 10.0 | 18.0 | 8.0 |
| PVPVI/PVNO | 0.5 | - | 0.3 | - |
| Protease | 1.0 | 1.0 | 1.0 | 0.5 |
| Lipase | 0.4 | - | - | 0.4 |
| Amylase | 0.1 | - | - | 0.1 |
| Cellulase | 0.1 | 0.2 | 0.2 | 0.1 |
| NOBS | - | 4.0 | - | 4.5 |
| PB1 | 1.0 | 5.0 | 1.5 | 6.0 |

| | A | B | C | D |
|--------------------|----------|----------|----------|----------|
| Sulfate | 4.0 | 5.0 | - | 5.0 |
| SRPI | - | 0.4 | - | - |
| ARP6 | - | 0.3 | 0.1(es) | - |
| ARP2 | - | - | - | 0.02(es) |
| Sud supressor | - | 0.5 | 0.5 | - |
| Misc/minor to 100% | | | | |

Example 7

The following granular detergent compositions were prepared in accord with the invention.

| | A | B | C |
|-----------------------|----------|----------|----------|
| Blown powder | | | |
| Zeolite A | 20.0 | - | 15.0 |
| STPP | - | 20.0 | - |
| Sulphate | - | - | 5.0 |
| Carbonate | - | - | 5.0 |
| TAS | - | - | 1.0 |
| LAS | 6.0 | 6.0 | 6.0 |
| C68AS | 2.0 | 2.0 | - |
| Silicate | 3.0 | 8.0 | - |
| MA/AA | 4.0 | 2.0 | 2.0 |
| CMC | 0.6 | 0.6 | 0.2 |
| Brightener 1 | 0.2 | 0.2 | 0.1 |
| DTPMP | 0.4 | 0.4 | 0.1 |
| STS | - | - | 1.0 |
| Spray on | | | |
| C45E7 | 5.0 | 5.0 | 4.0 |
| Silicone antifoam | 0.3 | 0.3 | 0.1 |
| Perfume | 0.2 | 0.2 | 0.3 |
| ARP6 | 0.1(s) | 0.05(s) | 0.08(s) |
| Dry additives | | | |
| QEA | - | - | 1.0 |
| Carbonate | 14.0 | 9.0 | 10.0 |
| PB1 | 1.5 | 2.0 | - |
| PB4 | 18.5 | 13.0 | 13.0 |
| TAED | 2.0 | 2.0 | 2.0 |
| QAS (I) | - | - | 1.0 |
| Photoactivated bleach | 15 ppm | 15 ppm | 15ppm |
| SKS-6 | - | - | 3.0 |
| Protease | 1.0 | 1.0 | 0.2 |
| Lipase | 0.2 | 0.2 | 0.2 |

| | A | B | C |
|---------------------|------|------|-----|
| Amylase | 0.4 | 0.4 | 0.2 |
| Cellulase | 0.1 | 0.1 | 0.2 |
| Sulfate | 10.0 | 20.0 | 5.0 |
| Misc/minors to 100% | | | |
| Density (g/litre) | 700 | 700 | 700 |

Example 8

The following detergent compositions, according to the present invention were prepared:

| | A | B | C |
|----------------------|----------|----------|----------|
| Blown Powder | | | |
| Zeolite A | 15.0 | 15.0 | 15.0 |
| Sulfate | 0.0 | 5.0 | 0.0 |
| LAS | 3.0 | 3.0 | 3.0 |
| QAS | - | 1.5 | 1.5 |
| DTPMP | 0.4 | 0.2 | 0.4 |
| EDDS | - | 0.4 | 0.2 |
| CMC | 0.4 | 0.4 | 0.4 |
| MA/AA | 4.0 | 2.0 | 2.0 |
| Agglomerates | | | |
| LAS | 5.0 | 5.0 | 5.0 |
| TAS | 2.0 | 2.0 | 1.0 |
| Silicate | 3.0 | 3.0 | 4.0 |
| Zeolite A | 8.0 | 8.0 | 8.0 |
| Carbonate | 8.0 | 8.0 | 4.0 |
| Spray On | | | |
| Perfume | 0.3 | 0.3 | 0.3 |
| C45E7 | 2.0 | 2.0 | 2.0 |
| C25E3 | 2.0 | - | - |
| ARP2 | 0.02(s) | - | - |
| Dry additives | | | |
| Citrate | 5.0 | - | 2.0 |
| Bicarbonate | - | 3.0 | - |
| Carbonate | 8.0 | 15.0 | 10.0 |
| TAED | 6.0 | 2.0 | 5.0 |
| PB1 | 14.0 | 7.0 | 10.0 |
| PEO | - | - | 0.2 |
| ARP1 | - | 0.2 | 0.08(ec) |
| Bentonite clay | - | - | 10.0 |
| Protease | 1.0 | 1.0 | 1.0 |

| | A | B | C |
|---------------------|----------|----------|----------|
| Lipase | 0.4 | 0.4 | 0.4 |
| Amylase | 0.6 | 0.6 | 0.6 |
| Cellulase | 0.6 | 0.6 | 0.6 |
| Silicone antifoam | 5.0 | 5.0 | 5.0 |
| Dry additives | | | |
| Sodium sulfate | 0.0 | 3.0 | 0.0 |
| Misc/minors to 100% | 100.0 | 100.0 | 100.0 |
| Density (g/litre) | 850 | 850 | 850 |

| | D | E | F | G | H |
|------------------------------|----------|----------|----------|----------|----------|
| Blown Powder | | | | | |
| STPP/ Zeolite A | 9.0 | 15.0 | 15.0 | 9.0 | 9.0 |
| Flocculating agent II or III | 0.5 | 0.2 | 0.9 | 1.5 | - |
| LAS | 7.5 | 23.0 | 3.0 | 7.5 | 7.5 |
| QAS | 2.5 | 1.5 | - | - | - |
| DTPMP | 0.4 | 0.2 | 0.4 | 0.4 | 0.4 |
| HEDP or EDDS | - | 0.4 | 0.2 | - | - |
| CMC | 0.1 | 0.4 | 0.4 | 0.1 | 0.1 |
| Sodium carbonate | 5.0 | 20.0 | 20.0 | 10.0 | - |
| Brightener | 0.05 | - | - | 0.05 | 0.05 |
| Clay I or II | - | 10.0 | - | - | - |
| STS | 0.5 | - | - | 0.5 | 0.5 |
| MA/AA | 1.5 | 2.0 | 2.0 | 1.5 | 1.5 |
| Agglomerates | | | | | |
| Suds suppresser (silicon) | 1.0 | 1.0 | - | 2.0 | 0.5 |
| Agglomerate | | | | | |
| Clay | 9.0 | - | - | 4.0 | 10.0 |
| Wax | 0.5 | - | - | 0.5 | 1.5 |
| Glycerol | 0.5 | - | - | 0.5 | 0.5 |
| Agglomerate | | | | | |
| LAS | - | 5.0 | 5.0 | - | - |
| TAS | - | 2.0 | 1.0 | - | - |
| Silicate | - | 3.0 | 4.0 | - | - |

| | | | | | |
|----------------------------------|-------|--------|-------|---------|-------|
| Zeolite A | - | 8.0 | 8.0 | - | - |
| Carbonate | - | 8.0 | 4.0 | - | - |
| Spray On | | | | | |
| Perfume | 0.3 | - | - | 0.3 | 0.3 |
| C45E7 or E9 | 2.0 | - | - | 2.0 | 2.0 |
| C25E3 or E4 | 2.0 | - | - | 2.0 | 2.0 |
| Dry additives | | | | | |
| Citrate or citric acid | 2.5 | - | 2.0 | 2.5 | 2.5 |
| Clay I or II | - | 5.0 | 5.0 | - | - |
| Flocculating agent I or II | - | - | - | - | 0.2 |
| Bicarbonate | - | 3.0 | - | - | - |
| Carbonate | 15.0 | - | - | 25.0 | 31.0 |
| TAED | 1.0 | 2.0 | 5.0 | 1.0 | - |
| Sodium perborate or percarbonate | 6.0 | 7.0 | 10.0 | 6.0 | - |
| SRP1, 2, 3 or 4 | 0.2 | 0.1 | 0.2 | 0.5 | 0.3 |
| CMC or nonionic cellulose ether | 1.0 | 1.5 | 0.5 | - | - |
| Protease | 0.3 | 1.0 | 1.0 | 0.3 | 0.3 |
| Lipase | - | 0.4 | 0.4 | - | - |
| Amylase | 0.2 | 0.6 | 0.6 | 0.2 | 0.2 |
| Cellulase | 0.2 | 0.6 | 0.6 | 0.2 | 0.2 |
| Silicone antifoam | - | 5.0 | 5.0 | - | - |
| Perfume (starch) | 0.2 | 0.3 | 1.0 | 0.2 | 0.2 |
| Speckle | 0.5 | 0.5 | 0.1 | - | 1.0 |
| NaSKS-6 (silicate 2R) | 3.5 | - | - | - | 3.5 |
| Photobleach | 0.1 | - | - | 0.1 | 0.1 |
| Soap | 0.5 | 2.5 | - | 0.5 | 0.5 |
| Sodium sulfate | - | 3.0 | - | - | - |
| ARP6 | 0.1 | 1.0(d) | 0.05 | 3.0(es) | 0.09 |
| Misc/minors to 100% | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Density (g/litre) | 850 | 850 | 850 | 850 | 850 |

Example 9

The following detergent formulations, according to the present invention were prepared:

| | A | B | C | D |
|--------------------------------|----------|----------|----------|----------|
| LAS | 18.0 | 14.0 | 24.0 | 20.0 |
| QAS | 0.7 | 1.0 | - | 0.7 |
| TFAA | - | 1.0 | - | - |
| C23E56.5 | - | - | 1.0 | - |
| C45E7 | - | 1.0 | - | - |
| C45E3S | 1.0 | 2.5 | 1.0 | - |
| STPP | 32.0 | 18.0 | 30.0 | 22.0 |
| Silicate | 9.0 | 5.0 | 9.0 | 8.0 |
| Carbonate | 11.0 | 7.5 | 10.0 | 5.0 |
| Bicarbonate | - | 7.5 | - | - |
| PB1 | 3.0 | 1.0 | - | - |
| PB4 | - | 1.0 | - | - |
| NOBS | 2.0 | 1.0 | - | - |
| DTPMP | - | 1.0 | - | - |
| DTPA | 0.5 | - | 0.2 | 0.3 |
| SRP 1 | 0.3 | 0.2 | - | 0.1 |
| MA/AA | 1.0 | 1.5 | 2.0 | 0.5 |
| CMC | 0.8 | 0.4 | 0.4 | 0.2 |
| PEI | - | - | 0.4 | - |
| Sodium sulfate | 20.0 | 10.0 | 20.0 | 30.0 |
| Mg sulfate | 0.2 | - | 0.4 | 0.9 |
| Protease | 0.8 | 1.0 | 0.5 | 0.5 |
| Amylase | 0.5 | 0.4 | - | 0.25 |
| Lipase | 0.2 | - | 0.1 | - |
| Cellulase | 0.15 | - | - | 0.05 |
| Photoactivated bleach (ppm) | 30ppm | 20ppm | - | 10ppm |
| ARP4 | 0.04(s) | 0.02(ec) | 0.1(s) | 0.01(es) |
| Perfume spray on | 0.3 | 0.3 | 0.1 | 0.2 |
| Brightener 1/2 | 0.05 | 0.2 | 0.08 | 0.1 |

| | A | B | C | D |
|---------------------|---|---|---|---|
| Misc/minors to 100% | | | | |

Example 10

The following liquid detergent formulations were prepared in accord with the invention (levels are given as parts per weight).

| | A | B | C | D | E |
|-------------------------|------|------|------|------|------|
| LAS | 11.5 | 8.8 | - | 3.9 | - |
| C25E2.5S | - | 3.0 | 18.0 | - | 16.0 |
| C45E2.25S | 11.5 | 3.0 | - | 15.7 | - |
| C23E9 | - | 2.7 | 1.8 | 2.0 | 1.0 |
| C23E7 | 3.2 | - | - | - | - |
| CFAA | - | - | 5.2 | - | 3.1 |
| TPKFA | 1.6 | - | 2.0 | 0.5 | 2.0 |
| Citric acid (50%) | 6.5 | 1.2 | 2.5 | 4.4 | 2.5 |
| Calcium formate | 0.1 | 0.06 | 0.1 | - | - |
| Sodium formate | 0.5 | 0.06 | 0.1 | 0.05 | 0.05 |
| Sodium cumene sulfonate | 4.0 | 1.0 | 3.0 | 1.18 | - |
| Borate | 0.6 | - | 3.0 | 2.0 | 2.9 |
| Sodium hydroxide | 5.8 | 2.0 | 3.5 | 3.7 | 2.7 |
| Ethanol | 1.75 | 1.0 | 3.6 | 4.2 | 2.9 |
| 1, 2 propanediol | 3.3 | 2.0 | 8.0 | 7.9 | 5.3 |
| Monoethanolamine | 3.0 | 1.5 | 1.3 | 2.5 | 0.8 |
| TEPAE | 1.6 | - | 1.3 | 1.2 | 1.2 |
| Protease | 1.0 | 0.3 | 1.0 | 0.5 | 0.7 |
| Lipase | - | - | 0.1 | - | - |
| Cellulase | - | - | 0.1 | 0.2 | 0.05 |
| Amylase | - | - | - | 0.1 | - |
| SRP1 | 0.2 | - | 0.1 | - | - |
| DTPA | - | - | 0.3 | - | - |
| PVNO | - | - | 0.3 | - | 0.2 |
| ARP1 | 0.3 | - | - | - | - |
| ARP2 | - | 0.04 | - | - | - |
| ARP3 | - | - | 0.3 | - | - |
| ARP4 | - | - | - | 0.04 | - |

| | A | B | C | D | E |
|-------------------|----------|----------|----------|----------|----------|
| ARP5 | - | - | - | - | 0.1 |
| Brightener 1 | 0.2 | 0.07 | 0.1 | - | - |
| Silicone antifoam | 0.04 | 0.02 | 0.1 | 0.1 | 0.1 |
| Water/minors | | | | | |

Example 11

The following liquid detergent formulations were prepared in accord with the invention (levels are given in parts per weight):

| | A | B | C | D | E | F | G | H |
|--------------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|
| LAS | 10.0 | 13.0 | 9.0 | - | 25.0 | - | - | - |
| C25AS | 4.0 | 1.0 | 2.0 | 10.0 | - | 13.0 | 18.0 | 15.0 |
| C25E3S | 1.0 | - | - | 3.0 | - | 2.0 | 2.0 | 4.0 |
| C25E7 | 6.0 | 8.0 | 13.0 | 2.5 | - | - | 4.0 | 4.0 |
| TFAA | - | - | - | 4.5 | - | 6.0 | 8.0 | 8.0 |
| APA | - | 1.4 | - | - | 3.0 | 1.0 | 2.0 | - |
| TPKFA | 2.0 | - | 13.0 | 7.0 | - | 15.0 | 11.0 | 11.0 |
| Citric acid | 2.0 | 3.0 | 1.0 | 1.5 | 1.0 | 1.0 | 1.0 | 1.0 |
| Dodecenyl/tetradecenyl succinic acid | 12.0 | 10.0 | - | - | 15.0 | - | - | - |
| Rape seed fatty acid | 4.0 | 2.0 | 1.0 | - | 1.0 | - | 3.5 | - |
| Ethanol | 4.0 | 4.0 | 7.0 | 2.0 | 7.0 | 2.0 | 3.0 | 2.0 |
| 1,2 Propanediol | 4.0 | 4.0 | 2.0 | 7.0 | 6.0 | 8.0 | 10.0 | 13.0 |
| Monoethanolamine | - | - | - | 5.0 | - | - | 9.0 | 9.0 |
| Triethanolamine | - | - | 8.0 | - | - | - | - | - |
| TEPAE | 0.5 | - | 0.5 | 0.2 | - | - | 0.4 | 0.3 |
| DTPMP | 1.0 | 1.0 | 0.5 | 1.0 | 2.0 | 1.2 | 1.0 | - |
| Protease | 0.5 | 0.5 | 0.4 | 0.25 | - | 0.5 | 0.3 | 0.6 |
| Alcalase | - | - | - | - | 1.5 | - | - | - |
| Lipase | - | 0.10 | - | 0.01 | - | - | 0.15 | 0.15 |
| Amylase | 0.25 | 0.25 | 0.6 | 0.5 | 0.25 | 0.9 | 0.6 | 0.6 |
| Cellulase | - | - | - | 0.05 | - | - | 0.15 | 0.15 |
| Endolase | - | - | - | 0.10 | - | - | 0.07 | - |
| SRP2 | 0.3 | - | 0.3 | 0.1 | - | - | 0.2 | 0.1 |
| Boric acid | 0.1 | 0.2 | 1.0 | 2.0 | 1.0 | 1.5 | 2.5 | 2.5 |

| | A | B | C | D | E | F | G | H |
|------------------|-----|------|-----|------|------|-----|------|------|
| Calcium chloride | - | 0.02 | - | 0.01 | - | - | - | - |
| Bentonite clay | - | - | - | - | 4.0 | 4.0 | - | - |
| Brightener 1 | - | 0.4 | - | - | 0.1 | 0.2 | 0.3 | - |
| Sud supressor | 0.1 | 0.3 | - | 0.1 | 0.4 | - | - | - |
| Opacifier | 0.5 | 0.4 | - | 0.3 | 0.8 | 0.7 | - | - |
| ARP1 | 0.3 | - | 0.1 | - | 0.05 | - | 0.1 | 0.08 |
| ARP2 | - | 0.04 | - | 0.02 | - | 0.1 | 0.02 | 0.1 |
| Water/minors | | | | | | | | |
| NaOH up to pH | 8.0 | 8.0 | 7.6 | 7.7 | 8.0 | 7.5 | 8.0 | 8.2 |

Example 12

The following liquid detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

| | A | B |
|----------------------|----------|----------|
| LAS | 27.6 | 18.9 |
| C45AS | 13.8 | 5.9 |
| C13E8 | 3.0 | 3.1 |
| Oleic acid | 3.4 | 2.5 |
| Citric acid | 5.4 | 5.4 |
| Sodium hydroxide | 0.4 | 3.6 |
| Calcium formate | 0.2 | 0.1 |
| Sodium formate | - | 0.5 |
| Ethanol | 7.0 | - |
| Monoethanolamine | 16.5 | 8.0 |
| 1,2 propanediol | 5.9 | 5.5 |
| Xylene sulfonic acid | - | 2.4 |
| TEPAE | 1.5 | 0.8 |
| Protease | 1.5 | 0.6 |
| PEG | - | 0.7 |
| Brightener 2 | 0.4 | 0.1 |
| Perfume spray on | 0.5 | 0.3 |
| ARP1 | 0.3 | - |
| ARP6 | - | 0.4 |
| Water/minors | | |

Example 13

The following is a composition in the form of a tablet, bar, extrudate or granule in accord with the invention

| | A | B | C | D | E | F | G |
|---|------|------|------|------|------|------|------|
| Sodium C ₁₁ -C ₁₃ alkylbenzenesulfonate | 12.0 | 16.0 | 23.0 | 19.0 | 18.0 | 20.0 | 16.0 |
| Sodium C ₁₄ -C ₁₅ alcohol sulfate | | 4.5 | - | | - | - | 4.0 |
| C ₁₄ -C ₁₅ alcohol ethoxylate (3) sulfate | - | - | 2.0 | - | 1.0 | 1.0 | 1.0 |
| Sodium C ₁₄ -C ₁₅ alcohol ethoxylate | 2.0 | 2.0 | - | 1.3 | - | - | 5.0 |
| C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt | | | - | - | 1.0 | 0.5 | 2.0 |
| Tallow fatty acid | | | - | - | - | - | 1.0 |
| Sodium tripolyphosphate / Zeolite | 23.0 | 25.0 | 14.0 | 22.0 | 20.0 | 10.0 | 20.0 |
| Sodium carbonate | 25.0 | 22.0 | 35.0 | 20.0 | 28.0 | 41.0 | 30.0 |
| Sodium Polyacrylate (45%) | 0.5 | 0.5 | 0.5 | 0.5 | - | - | - |
| Sodium polyacrylate/maleate polymer | - | - | 1.0 | 1.0 | 1.0 | 2.0 | 0.5 |
| Sodium silicate (1:6 ratio NaO/SiO ₂)(46%) | 3.0 | 6.0 | 9.0 | 8.0 | 9.0 | 6.0 | 8.0 |
| Sodium sulfate | - | - | - | - | - | 2.0 | 3.0 |
| Sodium perborate/percarbonate | 5.0 | 5.0 | 10.0 | - | 3.0 | 1.0 | - |
| Poly(ethyleneglycol), MW ~4000 (50%) | 1.5 | 1.5 | 1.0 | 1.0 | - | - | 0.5 |
| Sodium carboxy methyl cellulose | 1.0 | 1.0 | 1.0 | - | 0.5 | 0.5 | 0.5 |
| NOBS/ DOBS | - | 1.0 | - | - | 1.0 | 0.7 | - |

| | | | | | | | |
|---|------|--------|--------|---------|------|--------|------|
| TAED | 1.5 | 1.0 | 2.5 | - | 3.0 | 0.7 | - |
| SRP 1 | 1.5 | 1.5 | 1.0 | 1.0 | - | 1.0 | - |
| Clay I or II | 5.0 | 6.0 | 12.0 | 7.0 | 10.0 | 4.0 | 3.0 |
| Flocculating agent I or III | 0.2 | 0.2 | 3.0 | 2.0 | 0.1 | 1.0 | 0.5 |
| Humectant | 0.5 | 1.0 | 0.5 | 1.0 | 0.5 | 0.5 | - |
| Wax | 0.5 | 0.5 | 1.0 | - | - | 0.5 | 0.5 |
| Moisture | 7.5 | 7.5 | 6.0 | 7.0 | 5.0 | 3.0 | 5.0 |
| Magnesium sulphate | - | - | - | - | - | 0.5 | 1.5 |
| Chelant | - | - | - | - | 0.8 | 0.6 | 1.0 |
| Enzymes, including amylase, cellulase, protease and lipase | - | - | - | - | 2.0 | 1.5 | 2.0 |
| Speckle | 2.5 | 4.1 | 4.2 | 4.4 | 5.6 | 5.0 | 5.2 |
| ARP1 | 0.3 | 3.0(d) | - | - | - | - | - |
| ARP6 | 0.08 | 0.1 | 3.0(d) | 1.5(es) | 0.05 | 1.0(d) | 0.05 |
| minors, e.g. perfume, PVP, PVPVI/PVNO, brightener, photo-bleach | 2.0 | 1.0 | 1.0 | 1.0 | 2.5 | 1.5 | 1.0 |

| | H | I | J | K |
|--|------|------|------|------|
| Sodium C ₁₁ -C ₁₃ alkylbenzenesulfonate | 23.0 | 13.0 | 20.0 | 18.0 |
| Sodium C ₁₄ -C ₁₅ alcohol sulfate | - | 4.0 | - | - |
| Clay I or II | 5.0 | 10.0 | 14.0 | 6.0 |
| Flocculating agent I or II | 0.2 | 0.3 | 0.1 | 0.9 |
| Wax | 0.5 | 0.5 | 1.0 | - |
| Humectant (glycerol/ silica) | 0.5 | 2.0 | 1.5 | - |
| C ₁₄ -C ₁₅ alcohol ethoxylate sulfate | - | - | - | 2.0 |
| Sodium C ₁₄ -C ₁₅ alcohol ethoxylate | 2.5 | 3.5 | - | - |
| C ₉ -C ₁₄ alkyl dimethyl hydroxy ethyl quaternary ammonium salt | - | - | - | 0.5 |
| Tallow fatty acid | 0.5 | - | - | - |
| Tallow alcohol ethoxylate (50) | - | - | - | 1.3 |
| Sodium tripolyphosphate | - | 41.0 | - | 20.0 |
| Zeolite A, hydrate (0.1-10 micron size) | 26.3 | - | 21.3 | - |

| | | | | |
|--|------|--------|---------|------|
| Sodium carbonate | 24.0 | 22.0 | 35.0 | 27.0 |
| Sodium Polyacrylate (45%) | 2.4 | - | 2.7 | - |
| Sodium polyacrylate/maleate polymer | - | - | 1.0 | 2.5 |
| Sodium silicate (1.6 or 2 or 2.2 ratio NaO/SiO ₂)(46%) | 4.0 | 7.0 | 2.0 | 6.0 |
| Sodium sulfate | - | 6.0 | 2.0 | - |
| Sodium perborate/ percarbonate | 8.0 | 4.0 | - | 12.0 |
| Poly(ethyleneglycol), MW ~4000 (50%) | 1.7 | 0.4 | 1.0 | - |
| Sodium carboxy methyl cellulose | 1.0 | - | - | 0.3 |
| Citric acid | - | - | 3.0 | - |
| NOBS/ DOBS | 1.2 | - | - | 1.0 |
| TAED | 0.6 | 1.5 | - | 3.0 |
| Perfume | 0.5 | 1.0 | 0.3 | 0.4 |
| SRP 1 | - | 1.5 | 1.0 | 1.0 |
| Moisture | 7.5 | 3.1 | 6.1 | 7.3 |
| Magnesium sulphate | - | - | - | 1.0 |
| Chelant | - | - | - | 0.5 |
| speckle | 1.0 | 0.5 | 0.2 | 2.7 |
| Enzymes, including amylase, cellulase, protease and lipase | - | 1.0 | - | 1.5 |
| minors, e.g. brightener, photo-bleach | 1.0 | 1.0 | 1.0 | 1.0 |
| ARP6 | 0.1 | 3.0(d) | 1.0(es) | 0.3 |

Example 14

The following laundry bar detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

| | A | B | C | D | E | F | G | H |
|-------------------|------|------|------|------|------|-------|------|------|
| LAS | - | - | 19.0 | 15.0 | 21.0 | 6.75 | 8.8 | - |
| C28AS | 30.0 | 13.5 | - | - | - | 15.75 | 11.2 | 22.5 |
| Sodium laurate | 2.5 | 9.0 | - | - | - | - | - | - |
| Zeolite A | 2.0 | 1.25 | - | - | - | 1.25 | 1.25 | 1.25 |
| Carbonate | 20.0 | 3.0 | 13.0 | 8.0 | 10.0 | 15.0 | 15.0 | 10.0 |
| Calcium carbonate | 27.5 | 39.0 | 35.0 | - | - | 40.0 | - | 40.0 |
| Sulfate | 5.0 | 5.0 | 3.0 | 5.0 | 3.0 | - | - | 5.0 |
| TSPP | 5.0 | - | - | - | - | 5.0 | 2.5 | - |
| STPP | 5.0 | 15.0 | 10.0 | - | - | 7.0 | 8.0 | 10.0 |
| Bentonite clay | - | 10.0 | - | - | 5.0 | - | - | - |
| DTPMP | - | 0.7 | 0.6 | - | 0.6 | 0.7 | 0.7 | 0.7 |
| CMC | - | 1.0 | 1.0 | 1.0 | 1.0 | - | - | 1.0 |
| Talc | - | - | 10.0 | 15.0 | 10.0 | - | - | - |
| Silicate | - | - | 4.0 | 5.0 | 3.0 | - | - | - |
| PVNO | 0.02 | 0.03 | - | 0.01 | - | 0.02 | - | - |
| MA/AA | 0.4 | 1.0 | - | - | 0.2 | 0.4 | 0.5 | 0.4 |
| SRP1 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Protease | - | 0.12 | - | 0.08 | 0.08 | - | - | 0.1 |
| Lipase | - | 0.1 | - | 0.1 | - | - | - | - |
| Amylase | - | - | 0.8 | - | - | - | 0.1 | - |
| Cellulase | - | 0.15 | - | - | 0.15 | 0.1 | - | - |
| PEO | - | 0.2 | - | 0.2 | 0.3 | - | - | 0.3 |
| Perfume | 1.0 | 0.5 | 0.3 | 0.2 | 0.4 | - | - | 0.4 |
| Mg sulfate | - | - | 3.0 | 3.0 | 3.0 | - | - | - |
| ARP1 | 0.3 | - | - | - | - | 0.5 | - | - |
| ARP2 | - | 0.04 | - | - | - | - | 0.08 | - |
| ARP3 | - | - | 0.3 | - | - | - | - | - |
| ARP4 | - | - | - | 0.04 | - | - | - | - |
| ARP6 | - | - | - | - | 0.1 | - | - | 0.05 |
| Brightener | 0.15 | 0.10 | 0.15 | - | - | - | - | 0.1 |

| | A | B | C | D | E | F | G | H |
|--------------------------------|---|------|------|------|------|---|---|------|
| Photoactivated bleach (ppm) | - | 15.0 | 15.0 | 15.0 | 15.0 | - | - | 15.0 |

Example 15

The following detergent additive compositions were prepared according to the present invention :

| | A | B | C |
|---------------------------------|------------|----------|----------|
| LAS | - | 5.0 | 5.0 |
| STPP | 30.0 | - | 20.0 |
| Zeolite A | - | 35.0 | 20.0 |
| PB1 | 20.0 | 15.0 | - |
| TAED | 10.0 | 8.0 | - |
| ARP1 | 0.3 | - | 0.1 |
| ARP2 | - | 0.04 | 0.02 |
| Protease | - | 0.3 | 0.3 |
| Amylase | - | 0.06 | 0.06 |
| Minors, water and miscellaneous | Up to 100% | | |

Example 18

The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm² using a standard 12 head rotary press:

| | A | B | C | D | E | F |
|-------------------------|------------|-------|-------|---------|-------|-------|
| STPP | - | 48.8 | 49.2 | 38.0 | - | 46.8 |
| Citrate | 26.4 | - | - | - | 31.1 | - |
| Carbonate | - | 5.0 | 14.0 | 15.4 | 14.4 | 23.0 |
| Silicate | 26.4 | 14.8 | 15.0 | 12.6 | 17.7 | 2.4 |
| ARP1 | 0.3 | - | - | - | 0.06 | - |
| ARP2 | - | 0.04 | - | - | - | 0.08 |
| ARP6 | - | - | 0.3 | 0.1(ec) | - | - |
| Protease | 0.058 | 0.072 | 0.041 | 0.033 | 0.052 | 0.013 |
| Amylase | 0.01 | 0.03 | 0.012 | 0.007 | 0.016 | 0.002 |
| Lipase | 0.005 | - | - | - | - | - |
| PB1 | 1.6 | 7.7 | 12.2 | 10.6 | 15.7 | - |
| PB4 | 6.9 | - | - | - | - | 14.4 |
| Nonionic | 1.5 | 2.0 | 1.5 | 1.65 | 0.8 | 6.3 |
| PAAC | - | - | 0.02 | 0.009 | - | - |
| MnTACN | - | - | - | - | 0.007 | - |
| TAED | 4.3 | 2.5 | - | - | 1.3 | 1.8 |
| HEDP | 0.7 | - | - | 0.7 | - | 0.4 |
| DTPMP | 0.65 | - | - | - | - | - |
| Paraffin | 0.4 | 0.5 | 0.5 | 0.55 | - | - |
| BTA | 0.2 | 0.3 | 0.3 | 0.3 | - | - |
| PA30 | 3.2 | - | - | - | - | - |
| MA/AA | - | - | - | - | 4.5 | 0.55 |
| Perfume | - | - | 0.05 | 0.05 | 0.2 | 0.2 |
| Sulphate | 24.0 | 13.0 | 2.3 | - | 10.7 | 3.4 |
| Weight of tablet | 25g | 25g | 20g | 30g | 18g | 20g |
| pH | 10.6 | 10.6 | 10.7 | 10.7 | 10.9 | 11.2 |
| Miscellaneous and water | Up to 100% | | | | | |

Example 19

The following liquid dishwashing detergent compositions of density 1.40Kg/L were prepared according to the present invention :

| | A | B | C | D |
|--|----------|----------|----------|----------|
| STPP | 17.5 | 17.5 | 17.2 | 16.0 |
| Carbonate | 2.0 | - | 2.4 | - |
| Silicate | 5.3 | 6.1 | 14.6 | 15.7 |
| NaOCl | 1.15 | 1.15 | 1.15 | 1.25 |
| Polygen/carbopol | 1.1 | 1.0 | 1.1 | 1.25 |
| Nonionic | - | - | 0.1 | - |
| NaBz | 0.75 | 0.75 | - | - |
| ARP3 | 0.3 | 0.5 | 0.05 | 0.1 |
| NaOH | - | 1.9 | - | 3.5 |
| KOH | 2.8 | 3.5 | 3.0 | - |
| pH | 11.0 | 11.7 | 10.9 | 11.0 |
| Sulphate, miscellaneous and water up to 100% | | | | |

Example 20

The following liquid rinse aid compositions were prepared according to the present invention :

| | A | B | C |
|-------------------------|------------|----------|----------|
| Nonionic | 12.0 | - | 14.5 |
| Nonionic blend | - | 64.0 | - |
| Citric | 3.2 | - | 6.5 |
| HEDP | 0.5 | - | - |
| PEG | - | 5.0 | - |
| SCS | 4.8 | - | 7.0 |
| Ethanol | 6.0 | 8.0 | - |
| ARP1 | 0.3 | - | 0.1 |
| ARP2 | - | 0.04 | 0.01 |
| pH of the liquid | 2.0 | 7.5 | / |
| Miscellaneous and water | Up to 100% | | |

Example 21

The following liquid dishwashing compositions were prepared according to the present invention :

| | A | B | C | D | E |
|---------------------------------------|------------|-------|-------|-------|-------|
| C17ES | 28.5 | 27.4 | 19.2 | 34.1 | 34.1 |
| Amine oxide | 2.6 | 5.0 | 2.0 | 3.0 | 3.0 |
| C12 glucose amide | - | - | 6.0 | - | - |
| Betaine | 0.9 | - | - | 2.0 | 2.0 |
| Xylene sulfonate | 2.0 | 4.0 | - | 2.0 | - |
| Neodol C11E9 | - | - | 5.0 | - | - |
| Polyhydroxy fatty acid amide | - | - | - | 6.5 | 6.5 |
| Sodium diethylene penta acetate (40%) | - | - | 0.03 | - | - |
| TAED | - | - | - | 0.06 | 0.06 |
| Sucrose | - | - | - | 1.5 | 1.5 |
| Ethanol | 4.0 | 5.5 | 5.5 | 9.1 | 9.1 |
| Alkyl diphenyl oxide disulfonate | - | - | - | - | 2.3 |
| Ca formate | - | - | - | 0.5 | 1.1 |
| Ammonium citrate | 0.06 | 0.1 | - | - | - |
| Na chloride | - | 1.0 | - | - | - |
| Mg chloride | 3.3 | - | 0.7 | - | - |
| Ca chloride | - | - | 0.4 | - | - |
| Na sulfate | - | - | 0.06 | - | - |
| Mg sulfate | 0.08 | - | - | - | - |
| Mg hydroxide | - | - | - | 2.2 | 2.2 |
| Na hydroxide | - | - | - | 1.1 | 1.1 |
| Hydrogen peroxide | 200ppm | 0.16 | 0.006 | - | - |
| ARP3 | 0.3 | - | 0.1 | - | 0.1 |
| ARP1 | - | 0.3 | - | 0.1 | 0.1 |
| Protease | 0.017 | 0.005 | .0035 | 0.003 | 0.002 |
| Perfume | 0.18 | 0.09 | 0.09 | 0.2 | 0.2 |
| Water and minors | Up to 100% | | | | |

Example 22

The following liquid hard surface cleaning compositions were prepared according to the present invention :

| | A | B | C | D | E |
|--------------------------------------|------------|-------|-------|-------|------|
| ARP2 | 0.04 | - | 0.08 | - | 0.01 |
| ARP3 | - | 0.3 | - | 0.125 | 0.1 |
| Amylase | 0.01 | 0.002 | 0.005 | - | - |
| Protease | 0.05 | 0.01 | 0.02 | - | - |
| Hydrogen peroxide | - | - | - | 6.0 | 6.8 |
| Acetyl triethyl citrate | - | - | - | 2.5 | - |
| DTPA | - | - | - | 0.2 | - |
| Butyl hydroxy toluene | - | - | - | 0.05 | - |
| EDTA* | 0.05 | 0.05 | 0.05 | - | - |
| Citric / Citrate | 2.9 | 2.9 | 2.9 | 1.0 | - |
| LAS | 0.5 | 0.5 | 0.5 | - | - |
| C12 AS | 0.5 | 0.5 | 0.5 | - | - |
| C10AS | - | - | - | - | 1.7 |
| C12(E)S | 0.5 | 0.5 | 0.5 | - | - |
| C12,13 E6.5 nonionic | 7.0 | 7.0 | 7.0 | - | - |
| Neodol 23-6.5 | - | - | - | 12.0 | - |
| Dobanol 23-3 | - | - | - | - | 1.5 |
| Dobanol 91-10 | - | - | - | - | 1.6 |
| C25AE1.8S | - | - | - | 6.0 | |
| Na paraffin sulphonate | - | - | - | 6.0 | |
| Perfume | 1.0 | 1.0 | 1.0 | 0.5 | 0.2 |
| Propanediol | - | - | - | 1.5 | |
| Ethoxylated tetraethylene pentaimine | - | - | - | 1.0 | - |
| 2, Butyl octanol | - | - | - | - | 0.5 |
| Hexyl carbitol** | 1.0 | 1.0 | 1.0 | - | - |
| SCS | 1.3 | 1.3 | 1.3 | - | - |
| pH adjusted to | 7-12 | 7-12 | 7-12 | 4 | - |
| Miscellaneous and water | Up to 100% | | | | |

*Na4 ethylenediamine diacetic acid

****Diethylene glycol monohexyl ether**

Example 23

The following spray composition for cleaning of hard surfaces and removing household mildew was prepared according to the present invention :

| | |
|--------------------|------------|
| ARP6 | 0.04 |
| Amylase | 0.01 |
| Protease | 0.01 |
| Na octyl sulfate | 2.0 |
| Na dodecyl sulfate | 4.0 |
| Na hydroxide | 0.8 |
| Silicate | 0.04 |
| Butyl carbitol* | 4.0 |
| Perfume | 0.35 |
| Water/minors | up to 100% |

***Diethylene glycol monobutyl ether**

Example 24

The following lavatory cleansing block compositions were prepared according to the present invention.

| | A | B | C |
|---|----------|----------|----------|
| C16-18 fatty alcohol/50EO | 80.0 | - | - |
| LAS | - | - | 80.0 |
| Nonionic | - | 1.0 | - |
| Oleoamide surfactant | - | 26.0 | - |
| Partially esterified copolymer of vinylmethyl ether and maleic anhydride, viscosity 0.1-0.5 | 5.0 | - | - |
| Polyethylene glycol MW 8000 | - | 39.0 | - |
| Water-soluble K-polyacrylate MW 4000-8000 | - | 12.0 | - |
| Water-soluble Na-copolymer of acrylamide (70%) and acrylic acid (30%) low MW | - | 19.0 | - |
| Na triphosphate | 10.0 | - | - |
| Carbonate | - | - | 8.0 |
| ARP2 | 0.04 | - | 0.01 |
| ARP3 | - | 0.25 | 0.1 |
| Dye | 2.5 | 1.0 | 1.0 |
| Perfume | 3.0 | - | 7.0 |
| KOH / HCL solution | | pH 6-11 | |

Example 25

The following toilet bowl cleaning composition was prepared according to the present invention.

| | A | B |
|---------------------------|------------|----------|
| C14-15 linear alcohol 7EO | 2.0 | 10.0 |
| Citric acid | 10.0 | 5.0 |
| ARP2 | 0.04 | - |
| ARP3 | - | 0.1 |
| DTPMP | - | 1.0 |
| Dye | 2.0 | 1.0 |
| Perfume | 3.0 | 3.0 |
| NaOH | pH 6-11 | |
| Water and minors | Up to 100% | |

Example 26

The following laundry bar detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

| | A | B | C | D | E |
|-----------------------------------|-------|-------|------|------|------|
| NaLAS | 7.0 | 6.45 | 6.0 | - | 15.0 |
| Coco fatty alcohol sulfate (CFAS) | 13.0 | 15.05 | 15 | 18.0 | 0.0 |
| Zeolite A | - | 0.975 | 2 | 1.0 | 2.0 |
| Carbonate | 5.0 | 12.00 | - | - | - |
| Calcium carbonate | 33.5 | 32.5 | 20 | 12.0 | 10.0 |
| Sulfate | 5.0 | 5.0 | - | - | - |
| STPP | 18.0 | 11.6 | 16.0 | 18.0 | 35 |
| DTPA | 0.5 | 0.5 | 0.9 | 5.8 | 0.9 |
| CMC | 0.6 | 0.36 | - | - | - |
| C12 Coco fatty alcohol | 1.5 | 1.0 | 1.0 | 1.0 | 1.0 |
| PVNO | - | 0.14 | - | - | - |
| AA/MA | 0.4 | 0.4 | - | - | - |
| Glycerine | - | 1.0 | - | - | - |
| SRP1 | 0.2 | 0.2 | - | - | - |
| TiO ₂ | 0.7 | 0.7 | 1.0 | 1.0 | 1.0 |
| Ca(OH) ₂ | 2.0 | - | - | - | - |
| Protease | 0.08 | 0.08 | - | - | - |
| Cellulase | 0.08 | 0.08 | - | - | - |
| Sulfuric Acid | - | - | 2.5 | - | 2.5 |
| Soda Ash | - | - | 15.0 | 15.0 | 15.0 |
| PB1 | - | - | 2.25 | 4.5 | - |
| Perfume | 1.0 | 0.5 | 0.35 | 0.5 | - |
| Sulfate | 5.0 | - | - | - | - |
| PEI | 0.5 | - | - | - | - |
| Perfume | 0.4 | - | - | - | - |
| ARP2 | - | - | - | 0.32 | - |
| ARP1 | - | - | - | - | 0.4 |
| ARP6 | 0.32 | 0.32 | 0.32 | - | - |
| Brightener | 0.225 | 0.2 | 0.2 | 0.2 | - |
| Total Moisture Content | - | - | - | 2.5 | - |

| | A | B | C | D | E |
|------------------------------|---------|---------|---------|---------|---------|
| Other conventional materials | Balance | Balance | Balance | Balance | Balance |

What is claimed is:

1. A laundry and cleaning composition comprising a deterative ingredient and a product of reaction between a primary and/or secondary amine compound and a perfume component selected from ketone, aldehyde, and mixtures thereof, characterised in that said amine compound has an Odor Intensity Index of less than that of a 1% solution of methylantranilate in dipropylene glycol, and the product of reaction has a Dry Surface Odor Index of more than 5.
2. A composition according to Claim 1, wherein said amine compound has the following empirical formula selected from:
$$B-(NH_2)_n; B-(NH)_n; B-(NH)_n-(NH_2)_n$$
wherein B is a carrier material, and each n is independently an index of value of at least 1.
3. A composition according to Claim 2, wherein said carrier material is selected from inorganic or organic carriers, preferably is an organic carrier.
4. A composition according to Claim 3, wherein the inorganic carrier is an amino functionalized polydi-alkylsiloxane.
5. A composition according to Claim 3, wherein said amine having organic carrier material B is selected from aminoaryl derivatives, polyamines, amino acids and derivatives, substituted amines and amides, glucamines, dendrimers, amino-substituted mono-, di-, oligo-, poly-saccharides and/or mixtures thereof.
6. A composition according to Claim 5, wherein said aminoaryl derivatives are aminobenzene derivatives, preferably alkyl or aryl esters of 4-amino benzoate compounds, preferably selected from ethyl-4-amino benzoate, phenylethyl-4-aminobenzoate, phenyl-4-aminobenzoate, 4-amino-N'-(3-aminopropyl)-benzamide, and mixtures thereof.
7. A composition according to Claim 5, wherein said polyamines are polyethyleneimines, 2,2',2"-triaminotriethylamine; 2,2'-diamino-

diethylamine; 3,3'-diamino-dipropylamine, 1,3 bis aminoethylcyclohexane; poly[oxy(methyl-1,2-ethanediyl)], α -(2-aminomethylethyl)- ω -(2-amino-methylethoxy)-; poly[oxy(methyl-1,2-ethanediyl)], α -hydro-)- ω -(2-amino-methylethoxy)-, ether with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol; C12 Sternamines; and mixtures thereof.

8. A composition according to Claim 5, wherein said amine compounds are aminoacids and derivatives, preferably selected from tyrosine, tryptophane, lysine, glutamic acid, glutamine, aspartic acid, arginine, asparagine, phenylalanine, proline, glycine, serine, histidine, threonine, methionine, tyrosine ethylate or phenyl ester, tryptophane ethylate or phenyl ester, glycine methylate, and mixture thereof, more preferably selected from tyrosine, tryptophane, and mixture thereof
9. A composition according to Claim 5, wherein said amine compounds are substituted amines and amides, preferably selected from nipecotamide, N-coco-1,3-propenediamine; N-oleyl-1,3-propenediamine; N-(tallow alkyl)-1,3-propenediamine; 1,4-diamino cyclohexane; 1,2-diamino-cyclohexane; 1,12-diaminododecane, and mixtures thereof.
10. A composition according to Claim 5, wherein said amine compounds are glucamines of formula $\text{H}_2\text{N}-\text{CH}_2-(\text{CH}(\text{OH}))_x-\text{CH}_2\text{OH}$, wherein one or several OH-function can be substituted, and wherein x is an integer of value 3 or 4.
11. A composition according to Claim 5, wherein said amine compound is selected from polyamidoamine dendrimers, polyethylenimine and/or polypropylenimine dendrimers, and diaminobutane polyamine DAB (PA)_x dendrimers with $x = 2^n \times 4$ and n being comprised between 0 and 4, and/or mixtures thereof.
12. A composition according to Claim 5, wherein said amine compound is selected from amino-substituted mono-saccharides in the acetal or ketal form of glucose, mannose, galactose and/or fructose; amino-substituted di-saccharides in the acetal or ketal form of lactose, maltose, sucrose and/or cellobiose; amino-substituted oligo-saccharides and/or amino-substituted

poly-saccharides of cyclodextrin, chitosan, cellulose, starch, guaran, mannan and/or dextran; and/or mixtures thereof.

13. A composition according to Claim 12 wherein said amino-substituted mono-, di-, oligo-, poly-saccharide is selected from Amino alginate, Diamino alginate, Hexanediamine alginate, dodecanediamine alginate, 6-amino-6-deoxy cellulose, O-ethylamine cellulose, O-methylamine cellulose, 3-amino-3-deoxy cellulose, 2-amino-2 deoxy cellulose, 2,3-diamino-2,3-dideoxy cellulose, 6-[N-(1,6-hexanediamine)]-6-deoxy cellulose, 6-[N-(1,12-dodecanediamine)]-6-deoxy cellulose, O-[methyl-(N-1,6-hexanediamine)] cellulose, O-[methyl-(N-1,12-dodecanediamine)] cellulose, 2,3-di-[N-(1,12-dodecanediamine)] cellulose, 2,3-diamino-2,3-deoxy alpha-cyclodextrin, 2,3-diamino-2,3-deoxy beta-cyclodextrin, 2,3-diamino-2,3-deoxy gamma-cyclodextrin, 6-amino-6-deoxy alpha-cyclodextrin, 6-amino-6-deoxy beta-cyclodextrin, O-ethyleamino beta-cyclodextrin, 6[N-(1,6-hexanediamino)-6-deoxy alpha cyclodextrin, 6[N-(1,6-hexanediamino)-6-deoxy beta cyclodextrin, Amino dextran, N-[di-(1,6-hexanediamine)] dextran, N-[di-(1,12-dodecanediamine)] dextran, 6-amino-6-deoxy-alpha-D-galactosyl-guaran, O-ethylamino guaran, Diamino guaran, 6-amino-6-deoxy-starch, O-ethylamino starch, 2,3-diamine-2,3-dideoxy starch, N-[6-(1,6-hexanediamine)]-6-deoxy starch, N-[6-(1,12-dodecanediamine)]-6-deoxy starch, 2,3-di-[N(1,6-hexanediamine)]-2,3-dideoxy starch, and/or mixtures thereof.
14. A composition according to any one of Claims 1-13, wherein said product of reaction is preformed before incorporation into the laundry and cleaning composition.
15. A composition according to any one of Claims 1-14, wherein said product of reaction is present in an amount of from 0.0001% to 10%, preferably from 0.001% to 5%, and more preferably from 0.01% to 2%, by weight of the composition.
16. A composition according to Claims 1-15, wherein said perfume is a perfume aldehyde selected from 1-decanal, benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-

octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadienal; alpha-n-amyl cinnamic aldehyde, alpha-n-hexyl cinnamic aldehyde, P.T. Bucinal, lyral, cymal, methyl nonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof.

17. A composition according to Claims 1-15, wherein said perfume is a perfume ketone selected from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-Ionone, Iso-E-Super, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof.
18. A composition according to Claims 1-15 wherein said perfume has an Odor Detection Threshold lower or equal to than 1ppm, more preferably lower than or equal to 10ppb.
19. A compositions according to Claim 18 wherein said perfume is selected from undecylenic aldehyde, undecalactone gamma, heliotropin, dodecalactone gamma, p-anisic aldehyde, para hydroxy-phenyl-butanone, cymal, benzyl acetone, ionone alpha, p.t.bucinal, damascenone, ionone beta and methyl-nonyl ketone, and/or mixtures thereof.
20. A method of delivering residual fragrance to a surface which comprises the steps of contacting said surface with a composition as defined in any one of Claims 1-19, and thereafter contacting the treated surface with a material so that the perfume is released.
21. A method according to Claim 20, wherein said material is water.
22. Use of a compound as defined in any one of Claims 1-19, for the manufacture of a laundry and cleaning composition for delivering residual fragrance on a surface on which it is applied.
23. Use according to Claim 22, wherein said surface is a fabric.
24. Use according to Claim 22, wherein said surface is a tile and/or ceramic.